

60/106968



11/04/98

Class	Subclass
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PATENT APPLICATION



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3. Request for Access 7/19/04

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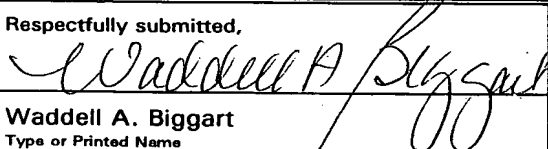
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SERIAL NUMBER 60/106,968 PROVISIONAL	FILING DATE 11/04/98	CLASS	GROUP ART UNIT 0000	ATTORNEY DOCKET NO. P52247	
APPLICANT	YOSHIAKI IKENOUE, TOKYO, JAPAN; HIROSHI KONUMA, CHIBA, JAPAN.				
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ADDRESS	SUGHRUE MION ZINN MACPEAK & SEAS 2100 PENNSYLVANIA AVENUE N W WASHINGTON DC 20037-3202				
	METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR				
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Attn: Assistant Commissioner for Patents, Washington, DC 20231

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

Docket Number	P52247		Type a plus sign (+) inside this box -->	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
IKENOUE, Yoshiaki	KONUMA, Hiroshi		Tokyo 105-8518 JAPAN Chiba 290-0067 JAPAN	
TITLE OF THE INVENTION (280 characters max)				
METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR				
CORRESPONDENCE ADDRESS				
SUGHRUE, MION, ZINN, MACPEAK & SEAS, PLLC 2100 Pennsylvania Avenue, N.W. Washington, D.C. 20037-3202 U.S.A. Tel: (202) 293-7060 Fax: (202) 293-7860				
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification*		Number of Pages <u>21</u>		<input type="checkbox"/> Small Entity Statement
<input checked="" type="checkbox"/> Japanese Language		Number of Claims <u>4</u>		<input type="checkbox"/> Other (specify)
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<input checked="" type="checkbox"/> A check or money order is enclosed to cover the Provisional Application filing fees. The Office is also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880.			Provisional Application Filing Fee Amount \$150.00	
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No. Yes, the name of the U.S. Government agency and the Government contract number are:				
Respectfully submitted, 			Date: November 4, 1998	
Waddell A. Biggart Type or Printed Name			Registration No. 24,861	

Additional inventors are being named on separately numbered sheets attached hereto.

PROVISIONAL APPLICATION FILING ONLY



PATENT APPLICATION SERIAL NO. _____

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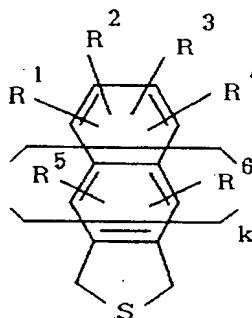
【書類名】 明細書

【発明の名称】 固体電解コンデンサの製造方法

【特許請求の範囲】

【請求項 1】 固体電解コンデンサの製造方法において、下記一般式 (I)

【化 1】



(式中、置換基 R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 はそれぞれ独立に H、炭素数 1 乃至 10 の直鎖状もしくは分岐状の飽和もしくは不飽和のアルキル基またはアルコキシ基またはアルキルエステル基、ハロゲン、ニトロ基、シアノ基、1 級、2 級または 3 級アミノ基、トリハロメチル基、フェニル基及び置換フェニル基からなる群から選ばれる一価基を表わす。 R^1 、 R^2 、 R^3 、 R^4 、 R^5 または R^6 の炭化水素鎖は互いに任意の位置で結合して、かかる基により置換を受けている炭素原子と共に少なくとも 1 つ以上の 3 乃至 7 員環の飽和または不飽和炭化水素の環状構造を形成する二価鎖を少なくとも 1 つ以上形成してもよい。 R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 のアルキル基、アルコキシ基、アルキルエステル基、またはそれらによって形成される環状炭化水素鎖にはカルボニル、エーテル、エステル、アミド、スルフィド、スルフィニル、スルホニル、イミノ等の結合を任意に含んでもよい。 k はジヒドロチオフェン環と置換基 R^1 乃至 R^4 を有するベンゼン環に囲まれた縮合環の数を表し、0 乃至 3 の整数値である。式中の縮合環には、窒素または N-オキシドを任意に含んでもよい。) で表される縮合ヘテロ多環式化合物を、単独またはドーバント能を有する他のアニオンと共に、誘電体層の金属酸化物多孔質内で酸化剤の作用によって重合することを特徴

とする固体電解コンデンサの製造方法。

【請求項2】 縮合ヘテロ多環式化合物が、ジヒドロイソチアナフテン、ジヒドロナフト〔2, 3-c〕チオフエン及びジヒドロチエノ〔3, 4-b〕キノキサリン誘導体の中から選ばれる単量体を少なくとも1つ以上用いることを特徴とする請求項1記載の固体電解コンデンサの製造方法。

【請求項3】 縮合ヘテロ多環式化合物が、1, 3-ジヒドロイソチアナフテン、5, 6-ジオキシメチレン-1, 3-ジヒドロイソチアナフテン、5, 6-ジメトキシ-1, 3-ジヒドロイソチアナフテン、1, 3-ジヒドロナフト〔2, 3-c〕チオフエン、1, 3-ジヒドロチエノ〔3, 4-b〕キノキサリン及び1, 3-ジヒドロチエノ〔3, 4-b〕キノキサリンから選ばれる単量体を少なくとも1つ以上用いることを特徴とする請求項1記載の固体電解コンデンサの製造方法。

【請求項4】 前記請求項1～3記載の重合体製造工程をそれぞれ同一誘電体層中で少なくとも2回以上繰り返して行うことを特徴とする固体電解コンデンサの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は、固体電解質に特定の導電性高分子組成物を含む固体電解コンデンサの製造方法に関するものであり、詳しくは電解コンデンサの小型化、高容量化、低インピーダンス化、そして耐湿負荷特性の良好かつ耐熱性の優れた電解コンデンサの製造方法に関する。

【0002】

【従来の技術】

固体電解コンデンサは、エッチング処理された比表面積の大きな金属箔からなる陽極基体に誘電体の酸化皮膜層が形成され、この外側に対向する電極として固体の半導電体層（以下、固体電解質と略する）が形成され、そして望ましくはさらに導電ペーストなどの導電体層が形成され、該コンデンサの基本素子が作製される。次いで、素子全体がエポキシ樹脂等で完全に封止され、コンデンサ部品と

して幅広く電気製品に使用されている。

【0003】

このうち、固体電解質には従来から、例えば、二酸化マンガンや二酸化鉛等の無機半導体材料、TCNQ錯塩、または π 共役系高分子を含む導電性有機物系のポリアニリン（特開昭61-239617号公報）、ポリピロール（特開昭61-240625号公報）、ポリチオフェン（特開平2-15611号公報）、ドーパントを含まないポリイソチアナフテン（特開昭62-118509号公報）、ドーパ状態のポリイソチアナフテン（特開昭62-118511号公報）等の使用が知られている。

【0004】

固体電解質層の形成方法については、従来から細孔あるいは空隙構造を有する金属表面の誘電体層上に、固体電解質を融解して形成する方法や誘電体層上で該固体電解質を産生する方法等が知られている。

【0005】

【発明が解決しようとする課題】

近年、電子機器の軽量化に伴い小型高容量の高周波特性の優れた低インピーダンスなコンデンサが求められている。この為、従来から誘電体皮膜上に各種固体電解質の形成が試みられ、このうち導電性金属酸化物や導電性高分子等が注目されている。その理由の1つとしては、固体電解質として電導度が充分高く改良できる等の期待がある。しかしながら、電導度が適正範囲より高すぎると、漏れ電流値が大きく上昇し結果ショートに至らし、また低いと周波数特性が悪くなり容量低下が大きくなるという問題点があり、電導度の適正範囲の制御並びに該固体電解質の熱的安定性等が開発課題の1つである。

【0006】

具体的に、ポリピロール等の導電性高分子を用いた従来のコンデンサでは、耐湿負荷によってコンデンサ特性が大きく変動するという問題点があった。また関連して耐熱性への要求が大きく、例えばコンデンサ素子からコンデンサ部品に成型する際のハンダ耐熱性（リフロー性）も重要視され、耐熱性の高いコンデンサ素子が求められている。即ち、従来技術においては固体電解質及びその製造方法

に問題があった。

【0007】

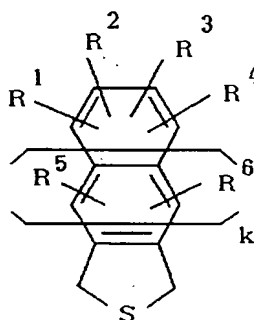
【課題を解決するための手段】

本発明は、上記課題に鑑み鋭意検討した結果、特定の化学構造を有する縮合ヘテロ多環式化合物を、金属酸化物誘電体層の細孔構造表面及びその近傍で重合させることを特徴として固体電解コンデンサを製造した結果、リフロー耐熱性等に優れたコンデンサであることをはじめて見出し、本発明に至った。

【0008】

即ち、本発明は、一般式（I）

【化2】



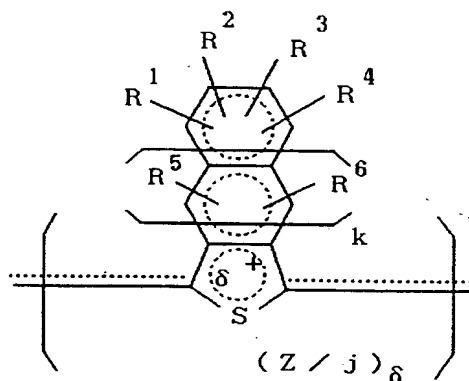
（式中、置換基 R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 はそれぞれ独立に H、炭素数 1 乃至 10 の直鎖状もしくは分岐状の飽和もしくは不飽和のアルキル基またはアルコキシ基またはアルキルエステル基、ハロゲン、ニトロ基、シアノ基、1 級、2 級または 3 級アミノ基、トリハロメチル基、フェニル基及び置換フェニル基からなる群から選ばれる一価基を表わす。 R^1 、 R^2 、 R^3 、 R^4 、 R^5 または R^6 の炭化水素鎖は互いに任意の位置で結合して、かかる基により置換を受けている炭素原子と共に、少なくとも 1 つ以上の 3 乃至 7 員環の飽和または不飽和炭化水素の環状構造を形成する二価鎖を少なくとも 1 つ以上形成してもよい。 R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 のアルキル基、アルコキシ基、アルキルエステル基、またはそれらによって形成される環状炭化水素鎖にはカルボニル、エーテル、エステル、アミド、スルフィド、スルフィニル、スルホニル、イミノ

等の結合を任意に含んでもよい。 k はジヒドロチオフェン環と置換基 R^1 乃至 R^4 を有するベンゼン環に囲まれた縮合環の数を表し、0乃至3の整数値である。式中の縮合環には、窒素またはN-オキシドを任意に含んでもよい。)で表される縮合ヘテロ多環式化合物を、単独またはドーバント能を有する他のアニオンと共に、誘電体層の金属酸化物多孔質内(細孔構造の表面または近傍)に導入し、次いで酸化剤を作用させて得られる重合体組成物を固体電解質として使用してなる固体電解コンデンサ及びその製造方法を提供するものである。但し、前記誘電体層中でのin-situ 化学重合の反応は、縮合ヘテロ多環式化合物と、またはアニオンと共に酸化剤を同時に誘電体層中に導入して重合反応を起こさせても良く、また最初に酸化剤を誘電体層表面に導入した後で縮合ヘテロ多環式化合物単独またはアニオンと共に導入して重合反応させてもよい。

[0009]

さらに本発明は、前記製造方法によって得られる重合体組成物の化学構造が、下記一般式(II)

【化3】



(式中、 R^1 、 R^2 、 R^3 、 R^4 、 R^5 、 R^6 及び k は前記一般式(I)と同じである。但し、 $k=0$ の誘導体のうち $R^1 \sim R^6$ の全ての置換基がHである化学構造を除く。また縮合環には窒素またはN-オキシドを任意に含んでもよく、また δ は0~1の範囲である。 Z は陰イオンを表し、 j は Z の価数を表し1または2である。)で表される構造単位を主鎖中に少なくとも1つ以上含む導電性重

合体組成物を備えたことを特徴とする固体電解コンデンサ及びその製造方法を提供するものである。

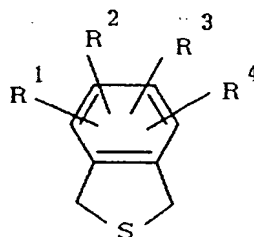
【0010】

さらに詳しくは、本発明は、対向する電極と一方の電極表面に金属酸化物の微細構造からなる誘電体層、及びその誘電体層上に前記記載の製造方法から製造される重合体組成物の固体電解質を具備した固体電解コンデンサ及び該製造方法に関するものである。

【0011】

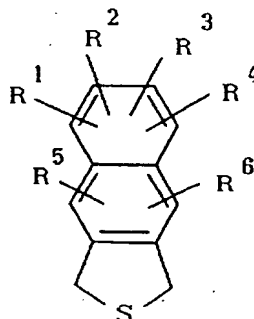
一般式（I）で表される縮合ヘテロ多環式化合物は、具体的に下記一般式（III））、

【化4】



（式中、 R^1 、 R^2 、 R^3 及び R^4 は一般式（I）と同じであり、また式中の縮合環には窒素またはN-オキシドを任意に含んでもよい。）で示される1,3-ジヒドロイソチアナフテン（別名、1,3-ジヒドロベンゾ[c]チオフェンとも言う）骨格を有する誘導体であり、また、下記一般式（IV）、

【化5】



(式中、置換基 R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 は一般式 (I) と同じであり、また式中の縮合環には窒素またはN-オキシドを任意に含んでもよい。) で示される1, 3-ジヒドロナフト [2, 3-c] チオフェン骨格を有する誘導体である。さらには、1, 3-ジヒドロアントラ [2, 3-c] チオフェン骨格を有する誘導体や1, 3-ジヒドロナフタセノ [2, 3-c] チオフェン骨格を有する誘導体も例示として挙げるができる。

【0012】

また、一般式 (I) で表される縮合ヘテロ多環式化合物の置換基 R^1 、 R^2 、 R^3 、 R^4 のうち、隣合う2つの置換基が相互に不飽和結合で結合しあって縮合系6員環(オルソ置換)を新たに形成する誘導体も含まれ、例えばその具体例としては、式中 $k=0$ の場合においては、1, 3-ジヒドロナフト [1, 2-c] チオフェン誘導体が、また式中 $k=1$ の場合では1, 3-ジヒドロフェナントラ [2, 3-c] チオフェン誘導体や1, 3-ジヒドロトリフェニロ [2, 3-c] チオフェン誘導体が、そして式中 $k=2$ の場合では1, 3-ジヒドロベンゾ [a] アントラセノ [7, 8-c] チオフェン誘導体等が含まれる。

【0013】

また、一般式 (I) で表される縮合ヘテロ多環式化合物の縮合環に窒素またはN-オキシドを任意に含んでもよく、例えば、式中 $k=0$ の場合では1, 3-ジヒドロチエノ [3, 4-b] キノキサリンや1, 3-ジヒドロチエノ [3, 4-b] キノキサリン-4-オキシド、1, 3-ジヒドロチエノ [3, 4-b] キノキサリン-4, 9-ジオキシドを挙げるができる。

【0014】

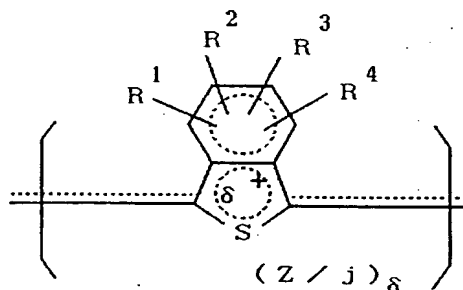
このように、一般式 (I) で表される縮合ヘテロ多環式化合物は、前記の如く1, 3-ジヒドロ型の縮合ヘテロ多環式化合物骨格を有し、本発明に記載の酸化反応プロセスによって容易に導電性重合体組成物を与えることができる。例えば、簡単な化学構造を有する代表例を下記に例示した(化合物(a)~化合物(t))を参照)。一般式 (I) で表される R^1 、 R^2 、 R^3 、 R^4 、 R^5 及び R^6 はそれぞれ独立に置換フェニル基を表すが、置換フェニル基の置換基にはCl、Br、I、F及び CF_3 から選ばれる一価基であり少なくとも1つ以上が置換され

た構造を有する。

【0015】

一方、前記重合体の製造方法において得られる重合体組成物の好ましい化学構造としては、一般式 (II) 記載の構造のうち、式中 $k=0$ の下記一般式 (V)

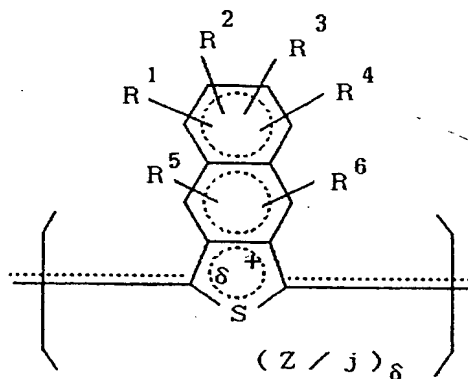
【化6】



(式中、 R^1 、 R^2 、 R^3 、 R^4 、 δ 、Z及びjは、一般式 (II) と同じであり、また縮合環には窒素またはN-オキシドを任意に含んでもよい。)

及び、式中 $k=1$ である下記一般式 (VI)

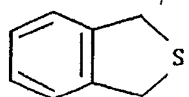
【化7】



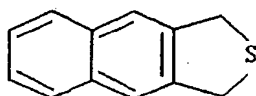
(式中、置換基 R^1 、 R^2 、 R^3 、 R^4 、 R^5 、 R^6 、 δ 、Z及びjは、一般式 (II) と同じであり、また縮合環には窒素またはN-オキシドを任意に含んでもよい。) を挙げることができる。

【化 8】

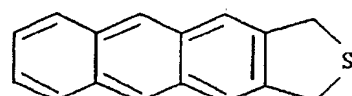
(a)



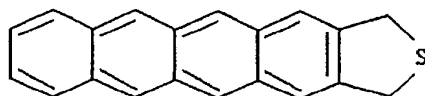
(b)



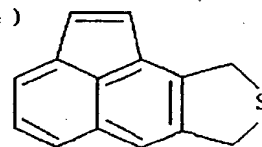
(c)



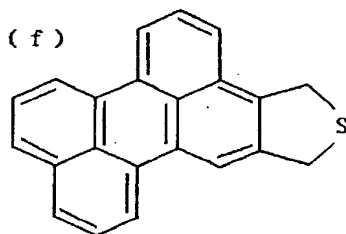
(d)



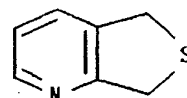
(e)



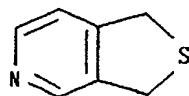
(f)



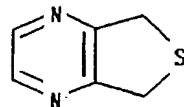
(g)



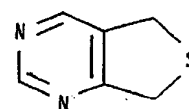
(h)



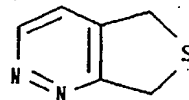
(i)



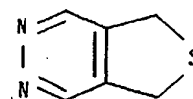
(j)



(k)

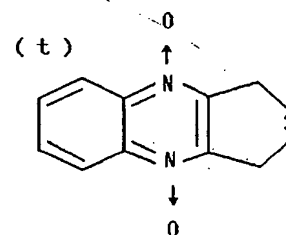
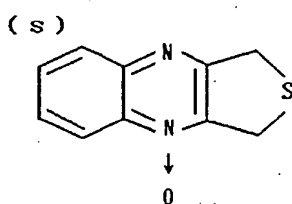
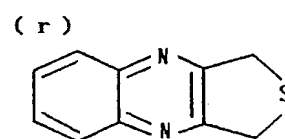
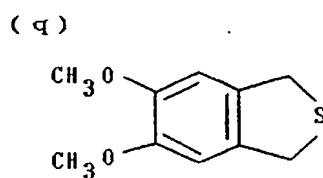
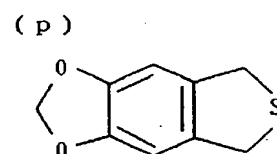
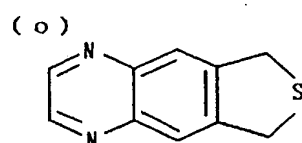
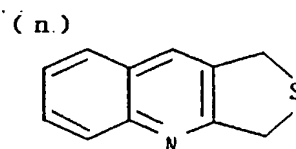
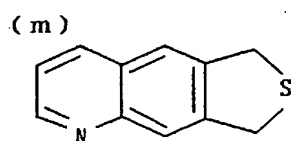


(l)



6010000-140000

【化 9】



【0016】

本発明に係わる重合方法は、縮合ヘテロ多環式化合物の酸化的脱水素反応（重合反応）が、金属酸化物誘電体層の細孔内において起こることが1つの特徴であり、また本使用環境での酸化剤が該環境であるが故に、より活性化（重合反応を促進）されて高電導度の重合体組成物を与える等の特徴を有する。この特徴は、

コンデンサ特性（容量、 $\tan \delta$ 、漏れ電流、インピーダンス及びリフロー耐熱性）で評価して見出したものである。すなわち、本発明の固体電解質（重合体組成物）の製造方法によれば、縮合ヘテロ多環式化合物の脱水素的酸化反応（4電子酸化）が、金属酸化物表面または近傍で溶媒の存在下または無溶媒下で短時間かつ簡便な反応条件で効果的に達成可能であって、従来既知のピロール類またはチオフェン類の脱水素的酸化反応（この場合2電子酸化重合）と比べても、産業上有用な固体電解コンデンサ特性を提供することができる。前記誘電体層中でのin-situ 化学重合の促進効果は、該誘電体の複雑な微細構造の寄与または大きな比表面積による効果または酸化物薄膜の持つ表面自由エネルギーの寄与等が考えられるが原理は定かではない。

【0017】

これまで重合体の製造方法に関する公知な方法としては、例えば、特開昭63-118323号公報及び特開平2-242816号公報において、1,3-ジヒドロイソチアナフテン構造を有する単量体が酸化剤の存在下で酸化的に重合される方法が開示されている。しかしながら、これらは単なる高分子化学の重合方法の例示であり、金属酸化物表面での効果を利用する本発明記載の化学反応プロセス（In-Situ 化学重合法）については全く記載されていない。また、Synthetic Metals 誌（16巻、379～380頁、1986年）においては、1,3-ジヒドロイソチアナフテン構造を有する単量体を酸素と酸化剤の共存下で酸化的に重合する方法が開示されているが、これも単なる合成反応の例示である。特開昭62-118509号公報及び特開昭62-118511号公報においては、重合体は電気化学的に重合されたものを固体電解質として利用したものであり、製造プロセスが本発明と異なる。そして、またコンデンサ特性が本発明と異なる。

【0018】

次に、本発明の第2目的として、高容量化を図る方法を提供することができる。即ち、本発明によれば、直接金属酸化物箔（例えば、アルミニウム化成箔）中で該単量体を単独または他のドーパント能を有するアニオンと共に、酸化剤の投入によって脱水素的4電子酸化反応（重合）を段階的に活用して、重合体組成物

を箔中に効果的に充填形成することができる方法を提供する。具体的には、縮合ヘテロ多環式化合物の重合において、先ず細孔構造を有する金属酸化物表面に酸化剤を溶液法による塗布、または気相法による昇華、蒸着等による方法で担持活性化させ、次いでまた必要に応じてドーパント能を有する他のアニオンを供与する化合物と共に縮合ヘテロ多環式化合物を微細構造表面に導入することによって、該重合体組成物を誘電体層上または近傍に形成するプロセスを提供するものである。これを繰り返し段階的に行うことにより、重合体組成物の固体電解質を細孔内部に効果的に充填形成する方法を作りだすことができる。これにより、固体電解質層内における導電パスの均一性が格段に改善でき、また細孔内部の不要な応力形成を防止（誘電体層の破壊防止）でき、結果的に高容量かつ低インピーダンスの優れたコンデンサ特性を実現することができるものである。

【0019】

さらに、本発明の第3の目的として、ハンダ耐熱性（熱安定性）の優れた方法を提供することができる。即ち、従来既知のポリピロール等からなる固体電解質を用いたコンデンサでは、高温高湿度でのLCR値の変動が大きく信頼性を悪くしていたが、本発明で示された化学構造の導電性組成物は、熱安定性に優れかつドープ状態の安定性がよく、さらにはこれらの重合性組成物を誘電体表面に段階的に析出させるために該重合体組成物の薄い膜質が何層にも重なった状態を作ることができ、該重合体が誘電体皮膜に対するダメージを生じない熱安定性に優れたコンデンサを提供することができる。

【0020】

本発明の製造方法において用いられる酸化剤は、脱水素的4電子酸化の酸化反応を充分行わせ得る酸化剤であれば良く、さらにその使用環境においてコンデンサ性能を向上させ得る酸化剤であれば良い。詳しくは、工業的に安価であり製造上取り扱いが容易である化合物が好まれる。具体的には、例えば FeCl_3 や FeClO_4 、 Fe （有機酸アニオン）塩等の Fe （III）系化合物類、または無水塩化アルミニウム／塩化第一銅、アルカリ金属過硫酸塩類、過硫酸アンモニウム塩類、過氧化物類、過マンガン酸カリウム等のマンガン類、2, 3-ジクロロ-5, 6-ジシアノ-1, 4-ベンゾキノン（DDQ）、テトラクロロ-1, 4-

ベンゾキノン、テトラシアノー１，４－ベンゾキノン等のキノン類、よう素、臭素等のハロゲン類、過酸、硫酸、発煙硫酸、三酸化硫黄、クロロ硫酸、フルオロ硫酸、アミド硫酸等のスルホン酸、オゾン等及びこれら複数の酸化剤の組み合わせが挙げられる。

【００２１】

この中で、前記 Fe（有機酸アニオン）塩を形成する有機酸アニオンの基本化合物としては、有機スルホン酸または有機カルボン酸、有機リン酸、有機ホウ酸等が挙げられる。有機スルホン酸の具体例としては、ベンゼンスルホン酸や p－トルエンスルホン酸、メタンスルホン酸、エタンスルホン酸、α－スルホ－ナフタレン、β－スルホ－ナフタレン、ナフタレンジスルホン酸、アルキルナフタレンスルホン酸（アルキル基としてはブチル、トリイソプロピル、ジ－tert－ブチル等）等が使用される。

【００２２】

一方、有機カルボン酸の具体例としては、酢酸、プロピオン酸、安息香酸、蔞酸等が挙げられる。さらに本発明においては、ポリアクリル酸、ポリメタクリル酸、ポリスチレンスルホン酸、ポリビニルスルホン酸、ポリビニル硫酸ポリ－α－メチルスルホン酸、ポリエチレンスルホン酸、ポリリン酸等の高分子電解質アニオンも使用されるが、これら有機スルホン酸または有機カルボン酸の例は単なる例示であってこの限りではない。また、前記アニオンの対カチオンは、 H^+ 、 Na^+ 、 K^+ 等のアルカリ金属イオン、または水素原子やテトラメチル基、テトラエチル基、テトラブチル基、テトラフェニル基等で置換されたアンモニウムイオンであるが、本発明においては特に限定を受けない。前記記載の酸化剤のうち、特に好ましくは３価の Fe 系化合物類、または塩化第一銅系、過硫酸アルカリ塩類、過硫酸アンモニウム塩類、マンガノ酸類、キノン類を含む酸化剤が好適に使用できる。

【００２３】

本発明の重合体組成物の製造方法において必要に応じて共存されるドーバント能を有するアニオンは、前記酸化剤から産生される酸化剤アニオン（酸化剤の還元体）を対イオンに持つ電解質化合物または他のアニオン系電解質を挙げるこ

ができる。具体的には例えば、 PF_6^- 、 SbF_6^- 、 AsF_6^- の如き5B族元素のハロゲン化物アニオン、 BF_4^- の如き3B族元素のハロゲン化物アニオン、 I^- (I_3^-)、 Br^- 、 Cl^- の如きハロゲンアニオン、 ClO_4^- の如きハロゲン酸アニオン、 AlCl_4^- や FeCl_4^- 、 SnCl_5^- 等の如きルイス酸アニオン、あるいは NO_3^- 、 SO_4^{2-} の如き無機酸アニオン、またはp-トルエンスルホン酸やナフタレンスルホン酸、炭素数1乃至5のアルキル置換スルホン酸、 CF_3SO_3^- 、 CH_3SO_3^- の如き有機スルホン酸アニオン、または CH_3COO^- 、 $\text{C}_6\text{H}_5\text{COO}^-$ のごときカルボン酸アニオン等のプロトン酸アニオンを挙げることができる。また、同じく、ポリアクリル酸、ポリメタクリル酸、ポリスチレンスルホン酸、ポリビニルスルホン酸、ポリビニル硫酸、ポリ- α -メチルスルホン酸、ポリエチレンスルホン酸、ポリリン酸等の高分子電解質アニオン等を挙げることができるが、必ずしも限定されるものではない。しかしながら、好ましくは高分子系または低分子系の有機スルホン酸化合物あるいはポリリン酸が挙げられ、望ましくは芳香族系スルホン酸化合物が用いられる。

【0024】

本発明のコンデンサの製造方法において用いられる一般式(I)の単量体濃度は、その化合物の置換基(種類)や溶媒等の種類によって異なるが、一般には 10^{-3} ~ 10 モル/リットルの範囲が望ましく、また 10^{-2} ~ 5 モル/リットルの範囲がさらに好ましい。また、反応温度は、それぞれ反応方法によって定められるもので特に限定できるものではないが、一般的には -70°C ~ 250°C の温度範囲で選ばれる。望ましくは、 0°C ~ 150°C であり、さらに 15 ~ 100°C の温度範囲で行われることが好ましい。

【0025】

本発明の製造方法において用いられる反応溶媒は、単量体あるいは酸化剤、ドーパント能を有する電解質を共に、またはそれぞれ単独に溶解可能な溶媒であれば良く、例えばテトラヒドロフラン(THF)やジオキサン、ジエチルエーテル等のエーテル類、あるいはジメチルホルムアミドやアセトニトリル、ベンゾニトリル、N-メチルピロリドン(NMP)、ジメチルスルホキシド(DMSO)等の非プロトン性極性溶媒、酢酸エチルや酢酸ブチル等のエステル類、クロロホル

ムや塩化メチレン等の非芳香族性の塩素系溶媒、ニトロメタンやニトロエタン、ニトロベンゼン等のニトロ化合物、あるいはメタノールやエタノール、プロパノール等のアルコール類、または蟻酸や酢酸、プロピオン酸等の有機酸または該有機酸の酸無水物（例、無水酢酸等）、水、あるいはこれらの混合溶媒を用いることができる。また、前記酸化剤または／及びドーパント能を有する電解質および単量体は、それぞれ単独に溶解した溶媒系、すなわち2液系もしくは3液系で取り扱って誘電体層内に該化合物を導入してもよい（重合反応に供してよい）。

【0026】

このようにして製造された固体導電体の電導度は、 $0.1 \sim 200 \text{ S/cm}$ の範囲であるが、望ましい条件では $1 \sim 100 \text{ S/cm}$ 、さらに好ましくは $10 \sim 100 \text{ S/cm}$ の範囲である。

【0027】

本発明の一方の電極にはアルミニウムまたはチタン、タンタル、ニオブあるいはこれらを基質となる合金系（等弁作用を有する）の箔、棒あるいはこれらを主成分とする焼結体等の公知な材料が使用される。これらの金属電極表面は、比表面積を大きくする目的で公知な方法によってエッチング処理や化成処理されて金属箔上に該金属系酸化皮膜層を形成されたものが用いられる。

【0028】

固体電解質の形成は、誘電体層上で形成する方法が好ましく、とりわけ本発明の耐熱性の優れた有機系導電体を細孔あるいは空隙構造を有する誘電体上に化学的に析出する方法が好ましい。さらに、半導体上に電気的接触をよくするために導電体層を設けることが好ましく、例えば、導電ペーストの固体、またはメッキや、金属蒸着、導電樹脂フィルム形成等が行われる。

【0029】

このように、本発明の製造方法から構成されるコンデンサは、例えば樹脂モールド、樹脂ケース、金属製の外装ケース、樹脂ディッピング等による外装により各種用途のコンデンサ製品とすることができる。

【0030】

【実施例】

以下、実施例及び比較例をあげて本発明を詳しく説明する。

(実施例1)

純度99.99%の厚さ100 μ mのアルミニウム箔を陽極として常法により電気化学的にその表面をエッチング処理して、多孔質アルミニウム箔を作製後、次いでアジピン酸アンモニウム液中で化成し、アルミニウム箔上に酸化アルミニウム層の誘電体薄膜を形成した。これを熱水でボイルし、再度化成することで誘電体薄膜を均質化させた。このように作製したアルミニウム箔を充分乾燥後、その細孔表面に酸化剤の硫酸鉄、0.1M濃度の水溶液を塗布して加熱乾燥（温度80℃）することで酸化剤を担持及び活性化させた。次いで、1,3-ジヒドロイソチアナフテンを5gとドデシルベンゼンスルホン酸ナトリウム（以下、DBSNaと略する）を0.1g溶かしたエタノール溶液中に前記アルミニウム箔を浸漬し気相中で80℃下10分加熱した。この溶媒の蒸発過程を伴うin-situ重合を20回繰り返して重合体組成物を製造した。表面上に堆積した重合体組成物の電導度を四端子で注意深く測定した結果、50S/cmであった。このように製作したコンデンサ素子の結果を表1に示した。但し、この時の容量及びtan δ は周波数が120Hzの値、インピーダンスは1000KHzの値である。

【0031】

(比較例1)

実施例1と同様な方法によって化成したアルミニウム箔を、以下の各成分の濃度が実施例1記載の場合と同一な濃度になるよう調整した3成分混合溶液（単量体、酸化剤及びドーパントは同じ）に浸漬させ、直ちに80℃、10分加熱するin-situ重合処理を20回繰り返してコンデンサ素子を作製した。表面上の電導度を四端子で注意深く測定した結果、 10^{-2} S/cmを示したが、コンデンサを作製して得られた容量は小さく、コンデンサ特性として充分ではなかった（表1中に併記）。

【0032】

(実施例2)

実施例 1 で使用した 1, 3-ジヒドロイソチアナフテンを 1, 3-ジヒドロナフト [2, 3-c] チオフェンに替えて、同様な製法によりコンデンサ素子を作製した。表面上に堆積した重合体組成物の電導度は、 20 S/cm (四端子法) を示し、同じくコンデンサ特性を測定した結果、表 1 中に記載の結果が得られた。

【0033】

(実施例 3)

実施例 1 で使用した 1, 3-ジヒドロイソチアナフテンを 5, 6-ジオキシメチレン-1, 3-ジヒドロイソチアナフテンに替え、また同実施例記載のドーパント (DBSN'a) を削除した単量体溶液で、同様なプロセスを行いコンデンサ素子を作製した。但し、in-situ 重合の処理条件は、 50°C 、10 分であった。表面上に堆積した重合体組成物の電導度は、 80 S/cm (四端子法) であり、表 1 記載の該コンデンサ特性が得られた。

【0034】

(比較例 2)

実施例 3 と同一の単量体及び酸化剤を、各成分濃度が実施例 3 と同一になるように調整した混合成分溶液に、実施例 1 と同様な方法によって作製したアルミニウム箔を浸漬し、実施例 3 と同じ温度 (50°C)、時間 (10 分) 及び同じ処理回数を行いコンデンサ素子を作製した。表面上の電導度は、 0.1 S/cm であり、コンデンサ特性としては、容量が小さかった (表 1 中に併記)。

【0035】

(実施例 4)

実施例 1 で使用した 1, 3-ジヒドロイソチアナフテンを 1, 3-ジヒドロチエノ [3, 4-b] キノキサリンに替え、加えてドーパントのドデシルベンゼンスルホン酸をナフタレンスルホン酸ナトリウム (以下、NSNa と略する) に替えて、実施例 1 と同様な製法によりコンデンサ素子を作製した。表面上に堆積した重合体組成物の電導度は、 5 S/cm (四端子法) であり、該コンデンサ特性を測定した結果、表 1 記載のデータが得られた。

【0036】

(実施例5)

実施例1で使用した1, 3-ジヒドロイソチアナフテンを5, 6-ジメトキシ-1, 3-ジヒドロイソチアナフテンに替え、DBSNaをNSNaに替えて、実施例1と同様な製法によりコンデンサ素子を作製した。但し、重合温度を70℃に、時間を20分に変更した。表面上に堆積した重合体組成物の電導度は、80 S/cm (四端子法) であり、該コンデンサ特性を測定した結果を表1に記載した。

【0037】

【表1】

コンデンサ特性

	容量 (μ F)	$\tan \delta$ (%)	漏れ電流 (μ A \cdot 10V値)	インピーダンス (Ω)
実施例1	9.9	0.88	0.09	0.078
実施例2	9.8	0.92	0.08	0.092
実施例3	10.1	0.80	0.08	0.052
実施例4	9.9	0.95	0.06	0.080
実施例5	10.2	0.86	0.06	0.055
比較例1	4.8	2.50	10.50	0.95
比較例2	6.7	2.30	8.65	0.67

【0038】

(比較例3)

前記実施例1～5及び比較例1、2の製造方法で製作されたコンデンサを各10個ずつ用い、リフロー処理前後の特性比較を行った。

【表 2】

リフロー耐熱性の試験結果（表中は素子10個当たりの製品合格数）

	リフロー処理前	リフロー処理後
実施例1で製造された素子	10	10
実施例2で製造された素子	9	7
実施例3で製造された素子	10	9
実施例4で製造された素子	10	10
実施例5で製造された素子	10	10
比較例1で製造された素子	3	0
比較例2で製造された素子	2	1

【0039】

（参考例1）

従来技術で製造された重合体組成物の電導度測定

Synthetic Metals 誌（16巻、379～380頁、1986年）記載の手法に従って、1, 3-ジヒドロイソチアナフテン単量体（融点23℃）をニトロベンゼン中50℃下、酸素及び塩化鉄（酸化剤）の存在下で溶液重合し、得られた重合体の電導度を測定したところ0.1 S/cmと低く、コンデンサの固体電解質として好ましい電導度ではなかった。

【0040】

【発明の効果】

本発明の製造方法により製造される固体電解コンデンサは、簡便な化学重合法で形成できる耐熱性の優れた高導電性高分子を固体電解質として具備することを特徴とし、その結果高容量かつ低インピーダンスな耐湿負荷特性の良好な耐熱性固体電解質コンデンサを与える。

【図面の簡単な説明】

【図1】

箔を用いた本発明に係わるコンデンサの代表的な縦断面図である。

【符号の説明】

- 1 箔
- 2 細孔
- 3 アルミニウムの酸化物層
- 4 固体電解質

[illegible]

- 20

【要約】

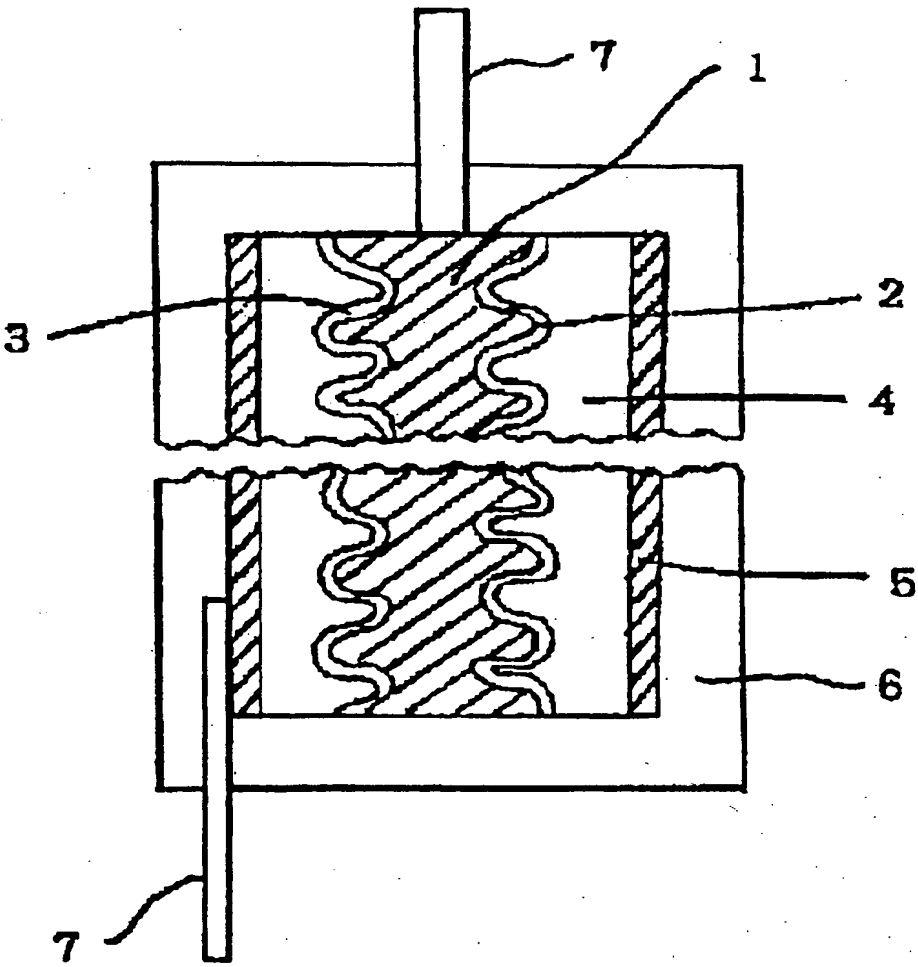
【解決手段】 非作用金属上に形成した酸化皮膜層表面に導電性重合体組成物を形成してなる固体電解コンデンサにおいて、前記酸化皮膜層表面または近傍で、酸化剤を単独またはドーパント能を有する他のアニオンとの共存下で使用するにより、1, 3-ジヒドロチオフェン環を有する特定化学構造の縮合ヘテロ多環式化合物を効果的に重合することを特徴とする固体電解コンデンサの製造方法を提供する。

【選択図】 なし

【書類名】

図面

【図 1】



50106965-110498



ATTN: BOX PROVISIONAL APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Provisional Application of

IKENOUE, Yoshiaki and KONUMA, Hiroshi

Provisional Appln. No.: 60/106,968

Filed: November 4, 1998

For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

REQUEST FOR CORRECTED PROVISIONAL APPLICATION FILING RECEIPT

ATTN: BOX PROVISIONAL APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

We enclose a copy of the Provisional Application Filing Receipt for the above-identified provisional application and request a correction as follows:

TITLE METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

The requested changes are supported by the application transmittal letter filed November 4, 1998 and the verified English language translation filed simultaneously herewith.

This error was caused by the PTO and therefore no fee is necessary.

Respectfully submitted,

Waddell A. Biggart
Waddell A. Biggart
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB:tnj
Date: May 10, 1999

PTO-103P
(Rev. 8-95)

PROVISIONAL APPLICATION
FILING RECEIPT



UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
ASSISTANT SECRETARY AND COMMISSIONER
OF PATENTS AND TRADEMARKS
Washington, D.C. 20231

APPLICATION NUMBER	FILING DATE	FIL FEE REC'D	ATTORNEY DOCKET NO.	DRWGS
60/106,968	11/04/98	\$150.00	P522247	1

SUGHRUE MION ZINN
MACPEAK & SEAS
2100 PENNSYLVANIA AVENUE N W
WASHINGTON DC 20037-3202



Receipt is acknowledged of this Provisional Application. This Provisional Application will not be examined for patentability. Be sure to provide the PROVISIONAL APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION when inquiring about this application. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please write to Box Provisional Application within 10 days of receipt. Please provide a copy of the Provisional Application Filing Receipt with the changes noted thereon. This Provisional Application will automatically be abandoned twelve (12) months after its filing date and will not be subject to revival to restore it to pending status beyond a date which is after twelve (12) months from its filing date.

Applicant(s) YOSHIKI IKENOUE, TOKYO, JAPAN; HIROSHI KONUMA, CHIBA, JAPAN.

TITLE
METHOD FOR PRODUCING SOLID ~~ELECTROLYTIC~~ CAPACITOR
ELECTROLYTIC



UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARK
Washington, D.C. 20231

APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO./TITLE
06/106,968	11/04/98	IKENQUE	Y P522247

SUGHRUE MION ZINN
MACPHEE & SEAS
2100 PENNSYLVANIA AVENUE N.W.
WASHINGTON DC 20037-3202

0252/0629

NOT ASSIGNED

0000

DATE MAILED: 06/29/99

NOTICE TO FILE MISSING PARTS OF PROVISIONAL APPLICATION
Filed Under 37 CFR 1.53 (c)
Filing Date Granted

An Application Number and Filing Date have been assigned to this Provisional Application. The items indicated below, however, are missing. Applicant is given TWO MONTHS FROM THE DATE OF THIS NOTICE within which to file all required items and pay fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a). If any of items 1 or 2 are indicated as missing, the SURCHARGE set forth in 37 CFR 1.16(l) of ☐ \$25.00 for a small entity in compliance with 37 CFR 1.27, or ☐ \$50.00 for a non-small entity, must also be timely submitted in reply to this NOTICE to avoid abandonment.

If all required items on this form are filed within the period set below, the total amount owed by applicant as a ☐ small entity (statement filed) ☐ non-small entity is \$ _____.

- ☐ 1. The statutory provisional application filing fee is:
 - ☐ missing.
 - ☐ insufficient.Applicant must submit \$ _____ to complete the basic filing fee and/or file a small entity statement claiming such status (37 CFR 1.27).
- ☐ 2. The provisional application cover sheet under 37 CFR 1.151(c)(1) is required identifying:
 - ☐ either the city and state or city and foreign country of the residence of each inventor.
 - ☐ the title of the invention.
- ☐ 3. The application was filed in a language other than English.
Applicant must file a verified English translation of the application, the \$130.00 set forth in 37 CFR 1.17(k), unless previously submitted, and a statement that the translation is accurate (37 CFR 1.52(d)).
- ☐ 4. A \$50.00 processing fee is required since your check was returned without payment (37 CFR 1.21 (m)).
- ☐ 5. Your filing receipt was mailed in error because your check was returned without payment.
- ☐ 6. The drawings contained in the application cannot be scanned or properly stored because they:
 - ☐ do not comply with the size requirements (8-1/2 by 11 inches or 21.0 by 29.7 cm).
 - ☐ are not clear enough or in permanent ink.
- ☐ 7. The specification cannot be scanned or properly stored. Page(s):
 - ☐ _____ do not contain writing on only one side of the page.
 - ☐ _____ do not comply with the size requirements (8-1/2 by 11 inches or 21.0 by 29.7 cm).
 - ☐ _____ are not clear enough or in permanent ink.Replacement pages, together with a statement that the replacement page(s) contain no new matter, are required.
- ☐ 8. Other: _____

Direct the reply and any questions about this notice to "Attention: Box Missing Parts."

A copy of this notice MUST be returned with the reply.

Customer Service Center
Initial Patent Examination Division (703) 308-1202



WABT mme
UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
Address: COMMISSIONER OF PATENTS AND TRADEMARK
Washington, D.C. 20231

APPLICATION NUMBER	FILING/RECEIPT DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO./TITLE
60/1062968	11/04/98	TKENQUE	Y P522247

SUGHRUE MION ZINN
MACPEAK & SEAS
2100 PENNSYLVANIA AVENUE N.W.
WASHINGTON DC 20007-3202

0252/0



NOT ASSIGNED

0000

DATE MAILED:

06/29/99

NOTICE TO FILE MISSING PARTS OF PROVISIONAL APPLICATION
Filed Under 37 CFR 1.53 (c)
Filing Date Granted

An Application Number and Filing Date have been assigned to this Provisional Application. The items indicated below, however, are missing. Applicant is given TWO MONTHS FROM THE DATE OF THIS NOTICE within which to file all required items and pay fees required below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a). If any of items 1 or 2 are indicated as missing, the SURCHARGE set forth in 37 CFR 1.16(l) of ☐ \$25.00 for a small entity in compliance with 37 CFR 1.27, or ☐ \$50.00 for a non-small entity, must also be timely submitted in reply to this NOTICE to avoid abandonment.

If all required items on this form are filed within the period set below, the total amount owed by applicant as a ☐ small entity (statement filed) ☐ non-small entity is \$ _____.

- ☐ 1. The statutory provisional application filing fee is:
- ☐ missing.
 - ☐ insufficient.
- Applicant must submit \$ _____ to complete the basic filing fee and/or file a small entity statement claiming such status (37 CFR 1.27).
- ☐ 2. The provisional application cover sheet under 37 CFR 1.151(c)(1) is required identifying:
- ☐ either the city and state or city and foreign country of the residence of each inventor.
 - ☒ the title of the invention.
- ☒ 3. The application was filed in a language other than English. Applicant must file a verified English translation of the application, the \$130.00 set forth in 37 CFR 1.17(k), unless previously submitted, and a statement that the translation is accurate (37 CFR 1.52(d)).
- ☐ 4. A \$50.00 processing fee is required since your check was returned without payment (37 CFR 1.21 (m)).
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 - ☐ _____ are not clear enough or in permanent ink.
- Replacement pages, together with a statement that the replacement page(s) contain no new matter, are required.
- ☐ 8. Other: _____

Direct the reply and any questions about this notice to "Attention: Box-Missing Parts."

A copy of this notice MUST be returned with the reply.

Customer Service Center
Initial Patent Examination Division (703) 308-1202

PART 2 - COPY TO BE RETURNED WITH RESPONSE

9202#

**ATTN: BOX PROVISIONAL PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Provisional Application of
IKENOUE, Yoshiaki and KONUMA, Hiroshi
Provisional Application No.: 60/106,968
Filed: November 4, 1998



For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

SUBMISSION OF VERIFIED ENGLISH TRANSLATION

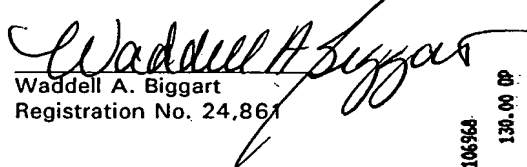
BOX PROVISIONAL PATENT APPLICATION
Attn: Office of National Application Review
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

In view of Applicants provisional application filing on November 4, 1998 in a foreign (Japanese) language, and since Applicants' attorney has not yet received the appropriate "Notice to File Missing Parts of Provisional Application Filed Under 37 CFR 1.53(b)(2)" for the above provisional application, submitted herewith is the verified English language translation (32 pages of specification + 1 pages of drawing(s)) for the above-mentioned provisional application previously filed in the Japanese language. Also enclosed please find a Request for Corrected Provisional Application Filing Receipt.

A check for the statutory fee of \$130.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.16 and 1.17 which may be required during the entire pendency of the provisional application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Respectfully submitted,


Waddell A. Biggart
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB:tnj
Date: May 10, 1999

05/11/1999 WABWJ 00000033 60106968 130.00 OP
01 FC1139

DECLARATION



I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/106,968 filed on November 4, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 20th day of January, 1999

Atsuko Ikeda
Atsuko Ikeda

[NAME OF DOCUMENT] Specification

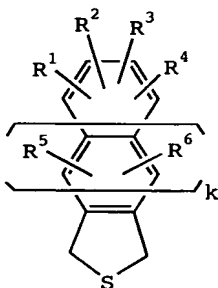
[TITLE OF THE INVENTION]

Method for Producing Solid Electrolytic Capacitor

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for producing a solid electrolytic capacitor, comprising polymerizing a condensed heteropolycyclic compound represented by the following formula (I):

[Chem. 1]



(wherein the substituents R¹, R², R³, R⁴, R⁵ and R⁶ each independently represents a monovalent group selected from the group consisting of H, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a trihalomethyl group, a phenyl group and a substituted phenyl group, the hydrocarbon chains of R¹, R², R³, R⁴, R⁵ and R⁶ may combine to each other at any site to form at

least one divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms to which the substituents are bonded, the alkyl group, the alkoxy group or the alkylester group of R¹, R², R³, R⁴, R⁵ or R⁶ or the cyclic hydrocarbon chain formed by the substituents may contain any of carbonyl, ether, ester, amide, sulfide, sulfinyl, sulfonyl and imino bonds, k represents a number of the condensed ring enclosed by the dihydrothiophene ring and the benzene ring having substituents R¹ to R⁴ and represents an integer of from 0 to 3, and the condensed ring may optionally contain nitrogen or N-oxide) alone or together with another anion having a dopant ability; within a metal oxide dielectric porous layer by the action of an oxidizing agent.

[Claim 2] The method for producing a solid electrolytic capacitor as claimed in claim 1, wherein the condensed heteropolycyclic compound uses at least one monomer selected from dihydroisothianaphthene, dihydro-naphtho[2,3-c]thiophene and dihydrothieno[3,4-b]quinoxaline derivatives.

[Claim 3] The method for producing a solid electrolytic capacitor as claimed in claim 1, wherein the condensed heteropolycyclic compound uses at least one monomer selected from 1,3-dihydroisothianaphthene, 5,6-

dioxymethylene-1,3-dihydroisothianaphthene, 5,6-dimethoxy-1,3-dihydroisothianaphthene, 1,3-dihydronaphtho[2,3-c]-thiophene, 1,3-dihydrothieno[3,4-b]quinoxaline and 1,3-dihydrothieno[3,4-b]quinoxaline.

[Claim 4] The method for producing a solid electrolytic capacitor as claimed in claims 1 to 3, wherein the polymer production process is repeated more than at least twice within the same dielectric layer.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method for producing a solid electrolytic capacitor containing a specific electrically conducting polymer composition as the solid electrolyte, more specifically, the present invention relates to an electrolytic capacitor capable of realizing miniaturization, high capacity and low impedance of the electrolytic capacitor and having good moisture resistance load and excellent heat resistance.

[0002]

[Background Art]

A solid electrolytic capacitor comprises an anode substrate comprising a metal foil subjected to etching treatment and having a large specific surface area. A basic device of the capacitor is manufactured by forming an oxide

dielectric film layer on the anode substrate, a solid semiconductor layer (hereinafter simply referred to as a solid electrolyte) as an opposing electrode outside the dielectric layer and preferably further an electric conductor layer such as an electrically conducting paste. Then, the device as a whole is completely sealed by an epoxy resin or the like and put into use as a capacitor part in electric products over a wide range.

[0003]

Of these basic elements, for the solid electrolyte, it has been heretofore known to use, for example, an inorganic semiconductor material such as manganese dioxide and lead dioxide or an electrically conducting organic material containing a TCNQ complex salt or a π -conjugated polymer such as polyaniline (JP-A-61-239617 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")), polypyrrole (JP-A-61-240625), polythiophene (JP-A-2-15611), polyisothianaphthene containing no dopant (JP-A-62-118509) or polyisothianaphthene in the doped state (JP-A-62-118511).

[0004]

[Problems to Be Solved by the Invention]

As the method for forming a solid electrolyte layer, a method of fusing a solid electrolyte into a porous or void structure of a dielectric layer on a metal surface to form

a solid electrolyte layer on the dielectric layer and a method of producing a solid electrolyte on a dielectric layer have been conventionally known.

[0005]

[Means to Solve the Problems]

As the electronic equipment is recently reduced in the weight, a compact capacitor having a high capacity, excellent high-frequency properties and a low impedance is being demanded. To cope with this, it has been heretofore attempted to form a solid electrolyte of various types on a dielectric film. Of these, electrically conducting metal oxides and electrically conducting polymers are drawing an attention. One of the reasons therefor is because the solid electrolyte may be improved to have a sufficiently high electric conductivity. However, there is a problem in that if the electric conductivity is higher than a proper range, the leakage current value greatly increases to cause short circuit, whereas if it is lower than the proper range, the frequency properties are deteriorated to cause large reduction in the capacity. Accordingly, a matter of problem to be studied and solved is to control a proper range of the electric conductivity and attain thermal stability of the solid electrolyte.

[0006]

To speak more specifically, conventional capacitors

using an electrically conducting polymer such as polypyrrole have a problem in that the capacitor properties greatly fluctuate according to the moisture resistance load. In this concern, the demand for heat resistance is keenly increased. For example, heat resistance in soldering (reflow property) at the time of forming a capacitor part from a capacitor device is important and a capacitor device having high heat resistance is being demanded. Conventional techniques are not satisfied with respect to the solid electrolyte and the production method thereof.

[0007]

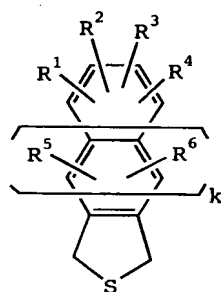
[Mode for Carrying Out the Invention]

As a result of extensive investigations to solve the above-described problems, the present inventors have first found that when a solid electrolytic capacitor is produced by polymerizing a condensed heteropolycyclic compound having a specific chemical structure on or in the vicinity of the surface of a metal oxide dielectric layer having a porous structure, a capacitor excellent in the reflow heat resistance and the like is produced. The present invention has been accomplished based on this finding.

[0008]

That is, the present invention provides a solid electrolytic capacitor using as a solid electrolyte a polymer composition obtained by introducing a condensed

heteropolycyclic compound represented by the following formula (I):



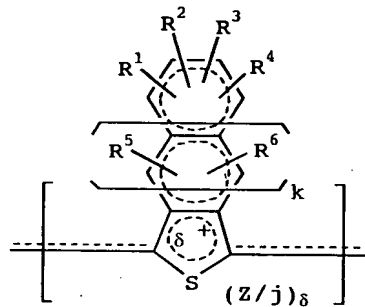
(wherein the substituents R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represents a monovalent group selected from the group consisting of H, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a trihalomethyl group, a phenyl group and a substituted phenyl group, the hydrocarbon chains of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may combine to each other at any site to form at least one divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms to which the substituents are bonded, the alkyl group, the alkoxy group or the alkylester group of R^1 , R^2 , R^3 , R^4 , R^5 or R^6 or the cyclic hydrocarbon chain formed by the substituents may contain any of carbonyl, ether, ester, amide, sulfide,

sulfinyl, sulfonyl and imino bonds, k represents a number of the condensed ring enclosed by the dihydrothiophene ring and the benzene ring having substituents R¹ to R^k and represents an integer of from 0 to 3, and the condensed ring may optionally contain nitrogen or N-oxide) alone or together with another anion having a dopant ability, into a metal oxide dielectric porous layer (on or in the vicinity of the surface of the porous structure) and acting thereon as an oxidizing agent, and also provides a production method of the electrolytic capacitor. The in-situ chemical polymerization reaction within the dielectric layer may be caused by introducing an oxidizing agent simultaneously with a condensed heteropolycyclic compound or further with an anion or by first introducing an oxidizing agent into the surface of the dielectric layer and then introducing a condensed heteropolycyclic compound alone or together with an anion.

[0009]

The present invention further provides a solid electrolytic capacitor, wherein the polymer composition obtained by the above-described production process is an electrically conducting polymer composition having a chemical structure of containing in the main chain at least one structural unit represented by the following formula (II):

[Chem. 3]



(wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and k are the same as in formula (I), provided that when $k=0$, derivatives having a chemical formula where the substituents R^1 to R^6 all are H are excluded, the condensed ring may optionally contain nitrogen or N-oxide, δ is from 0 to 1, Z represents an anion, and j represents a valency number of Z and is 1 or 2), and also provides a production method of the electrolytic capacitor.

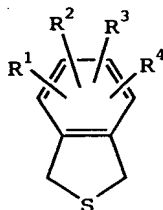
[0010]

More specifically, the present invention relates to a solid electrolytic capacitor comprising electrodes opposing to each other, a dielectric layer formed on the surface of one electrode and having a metal oxide porous structure, and a solid electrolyte formed on the dielectric layer and comprising a polymer composition obtained by the above-described production process, as well as to a production method of the electrolytic capacitor.

[0011]

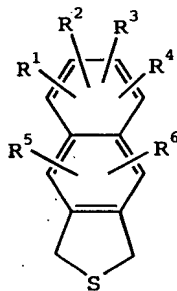
The condensed heteropolycyclic compound represented by formula (I) is specifically a derivative having a 1,3-dihydroisothianaphthene (or also called 1,3-dihydrobenzo-[c]thiophene) skeleton represented by the following formula (III):

[Chem. 4]



(wherein R¹, R², R³ and R⁴ are the same as in formula (I), and the condensed ring may optionally contain nitrogen or N-oxide) or a derivative having a 1,3-dihydronaphtho[2,3-c]thiophene skeleton represented by the following formula (IV):

[Chem. 5]



(wherein the substituents R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are the same as in formula (I), and the condensed ring may optionally contain nitrogen or N-oxide). Other examples include a derivative having a 1,3-dihydroanthra[2,3-c]thiophene skeleton and a derivative having a 1,3-dihydronaphthaceno[2,3-c]thiophene skeleton.

[0012]

Furthermore, derivatives, in which two adjacent substituents among the substituents R^1 , R^2 , R^3 and R^4 in the condensed heteropolycyclic compound represented by formula (I) are combined to each other through an unsaturated bond to newly form a condensed 6-membered ring (ortho-substitution), may also be used and specific examples thereof include, when $k=0$, a 1,3-dihydronaphtho[1,2-c]thiophene derivative, when $k=1$, a 1,3-dihydrophenanthra[2,3-c]thiophene derivative and a 1,3-dihydrotriphenylo[2,3-c]thiophene derivative, and when $k=2$, a 1,3-dihydrobenzo[a]anthraceno[7,8-c]thiophene derivative.

[0013]

The condensed ring in the condensed heteropolycyclic compound represented by formula (I) may optionally contain nitrogen or N-oxide and examples of such a condensed ring include, when $k=0$, 1,3-dihydrothieno[3,4-b]quinoxaline, 1,3-dihydrothieno[3,4-b]quinoxaline-4-oxide and 1,3-dihydrothieno[3,4-b]quinoxaline-4,9-dioxide.

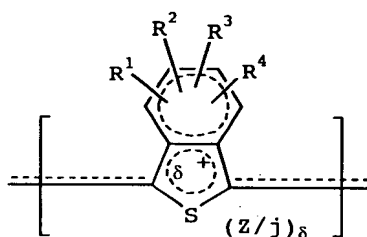
[0014]

As described in the foregoing, the condensed heteropolycyclic compound represented by formula (I) has the above-described 1,3-dihydro-type condensed heteropolycyclic compound skeleton and can easily provide an electrically conducting polymer composition by the oxidation reaction process described in the present invention. Representative examples of the compound having a simple chemical formula are described later (Compound (a) to Compound (t)). R^1 , R^2 , R^3 , R^4 , R^5 and R^6 in formula (I) each independently represents a substituted phenyl group. The substituted phenyl group includes a structure such that at least one monovalent group selected from Cl, Br, I, F and CF_3 is bonded as a substituent to a phenyl ring.

[0015]

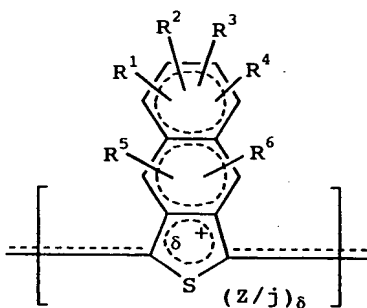
The polymer composition obtained by the above-described production process of a polymer preferably has a chemical structure of formula (II) where $k=0$, namely, formula (V):

[Chem. 6]



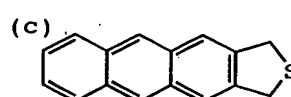
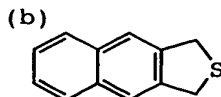
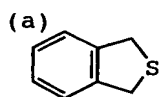
(wherein R^1 , R^2 , R^3 , R^4 , δ , Z and j are the same as in formula (II), and the condensed ring may optionally contain nitrogen or N-oxide) or where $k=1$, namely, formula (VI):

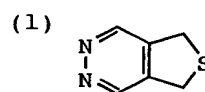
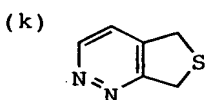
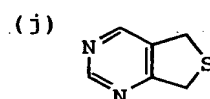
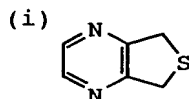
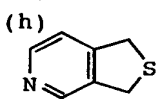
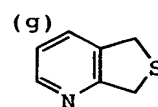
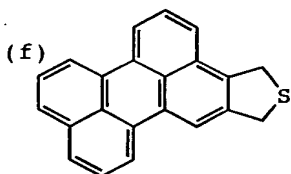
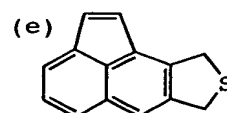
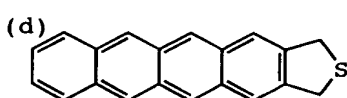
[Chem. 7]



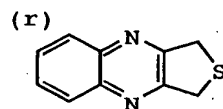
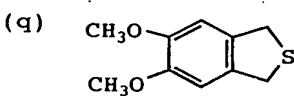
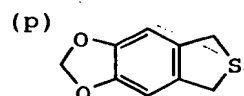
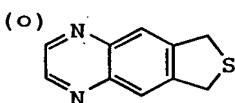
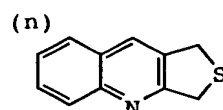
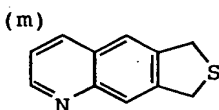
(wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , δ , Z and j are the same as in formula (II), and the condensed ring may optionally contain nitrogen or N-oxide).

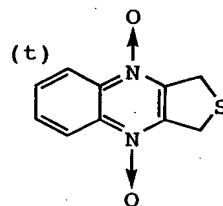
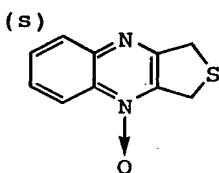
[Chem. 8]





[Chem. 9]





[0016]

The polymerization process according to the present invention is characterized in that the oxidative dehydrogenation reaction (polymerization reaction) of the condensed heteropolycyclic compound takes place within pores of a metal oxide dielectric layer and further that due to such an environment in using an oxidizing agent, the oxidizing agent is more activated (accelerates the polymerization reaction) to provide a polymer composition having a high electric conductivity. These characteristic features have been found as a result of evaluating the capacitor properties (e.g., capacity, $\tan \delta$, leakage current, impedance, reflow heat resistance). In other words, according to the production process of a solid polyelectrolyte (polymer composition) of the present invention, the dehydrogenative oxidation reaction (4 electron oxidation) of the condensed heteropolycyclic compound can be effectively achieved on or in the vicinity of the surface of a metal oxide in the presence or absence of a solvent under short-time and simple reaction

conditions. Therefore, as compared with the case using a conventionally known dehydrogenative oxidation reaction of a pyrrole or a thiophene (in this case, 2 electron oxidation polymerization), industrially useful solid electrolytic capacitor properties can be provided. The effect of accelerating the in-situ chemical polymerization in the dielectric layer may be considered to come out due to the complicated finely porous structure or large specific area of the dielectric or due to the surface free energy of the oxide thin film, however, the principle thereof is not yet elucidated.

[0017]

With respect to conventionally known examples of the method for producing a polymer, JP-A-63-118323 and JP-A-2-242816 disclose a method of oxidatively polymerizing a monomer having a 1,3-dihydroisothianaphthene structure in the presence of an oxidizing agent. This is, however, an example of a mere polymerization method in the polymer chemistry and the above-described patent publications are completely silent on the chemical reaction process (in-situ chemical polymerization process) using the effect on the surface of a metal oxide described in the present invention. Synthetic Metals, Vol. 16, pp. 379-380 (1986) discloses a method of oxidatively polymerizing a monomer having a 1,3-dihydroisothianaphthene structure in the presence of oxygen

and an oxidizing agent together, but this is also an example of mere synthesis reaction. Furthermore, JP-A-62-118509 and JP-A-62-118511 disclose use of an electrochemically polymerized polymer as a solid electrolyte and thus, these patent publications differ in the production process from the present invention. Moreover, the capacitor properties are different from those in the present invention.

[0018]

As the second object of the present invention, a method capable of achieving high capacity is provided. That is, according to the present invention, an oxidizing agent is charged together with the monomer alone or further with another anion having a dopant ability and by performing step by step the dehydrogenative 4 electron oxidation reaction (polymerization) directly within a metal oxide foil (for example, an formed aluminum foil), a polymer composition can be effectively filled into and formed within the foil. More specifically, the polymerization of a condensed heteropolycyclic compound proceeds through such a process that an oxidizing agent is carried and activated on the surface of a metal oxide having a porous structure by the coating according to a solution process or by the sublimation or evaporation according to a vapor phase process and then a condensed heteropolycyclic compound is

introduced into the surface of the fine structure, if desired, together with a compound capable of donating another anion having a dopant ability, thereby forming the polymer composition on or in the vicinity of the dielectric. By repeating this process step by step, a solid electrolyte comprising the polymer composition can be effectively filled and formed inside the pores. Due to this, homogeneity in the electric conducting path within the solid electrolyte layer can be remarkably improved, unnecessary formation of stresses inside the pores can be prevented (prevention of rupture of the dielectric layer) and as a result, excellent capacitor properties including high capacity and low impedance can be realized.

[0019]

As the third object of the present invention, a method capable of ensuring excellent soldering heat resistance (heat stability) is provided. Conventionally known capacitors using a solid electrolyte comprising polypyrrole or the like undergo large fluctuation in the LCR value at a high temperature and a high humidity and has poor reliability. However, the electrically conducting composition having a chemical formula shown in the present invention has excellent heat stability and exhibits good stability in the doped state. Furthermore, this polymer composition is step by step deposited on the surface of a

dielectric and accordingly, a structure of many polymer composition thin films being overlapped can be formed. Thus, the polymer can prevent damages of the dielectric film and a capacitor having excellent heat stability can be provided.

[0020]

The oxidizing agent for use in the production method of the present invention may be any oxidizing agent as far as oxidation reaction by dehydrogenative 4 electron oxidation can be satisfactorily effected and the capacitor performance can be improved in the use environment. In practice, compounds which are industrially inexpensive and easy to handle are preferred. Specific examples thereof include Fe(III) compounds such as FeCl_3 , FeClO_4 , and Fe (organic acid anion) salt, anhydrous aluminum chloride/cuprous chloride, alkali metal persulfates, ammonium persulfate salts, peroxides, manganese such as potassium permanganate, quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-1,4-benzoquinone and tetracyano-1,4-benzoquinone, halogens such as iodine and bromine, peracid, sulfuric acid, fuming sulfuric acid, sulfur trioxide, sulfonic acids such as chlorosulfuric acid, fluorosulfuric acid and amidosulfuric acid, ozone, and a combination of a plurality of these oxidizing agents.

[0021]

Examples of the base compound for the organic acid anion constituting the Fe (organic acid anion) salt include an organosulfonic acid, an organocarboxylic acid, an organophosphoric acid and an organoboric acid. Specific examples of the organosulfonic acid include benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, ethanesulfonic acid, α -sulfonaphthalene, β -sulfonaphthalene, naphthalenedisulfonic acid, alkylnaphthalenesulfonic acid (examples of the alkyl group include butyl, triisopropyl and di-t-butyl, etc.).

[0022]

Specific examples of the organocarboxylic acid include acetic acid, propionic acid, benzoic acid and oxalic acid. Furthermore, in the present invention, a polyelectrolyte anion such as polyacrylic acid, polymethacrylic acid, polystyrenesulfonic acid, polyvinylsulfonic acid, polyvinylsulfuric acid, poly- α -methylsulfonic acid, polyethylenesulfonic acid and polyphosphoric acid may also be used. However, these are described only for the purpose of illustrating examples of the organosulfonic acid and the organocarboxylic acid and the present invention is by no means limited thereto. The counter cation of the above-described anion is not particularly limited in the present invention and examples thereof include H^+ , alkali metal ion

such as Na^+ and K^+ , and ammonium ion substituted by a hydrogen atom, a tetramethyl group, a tetraethyl group, a tetrabutyl group or a tetraphenyl group. Of these oxidizing agents, oxidizing agents containing a trivalent Fe compound, cuprous chloride, a persulfuric acid alkali salt, an ammonium persulfate, a manganic acid or a quinone are suitably used.

[0023]

Examples of the anion having a dopant ability which is allowed to be present together, if desired, in the production process of the polymer composition of the present invention include electrolytic compounds comprised of anion of oxidizing agent (reductant of the oxidizing agent) produced from the above-described oxidizing agent as a counter anion, and other anionic electrolytes. Specific examples thereof include Group 5B element halide anions such as PF_6^- , SbF_6^- and AsF_6^- , Group 3B element halide anions such as BF_4^- , halogen anions such as I^- , Br^- and Cl^- , halogen acid anions such as ClO_4^- , Lewis acid anions such as AlCl_4^- , FeCl_4^- and SnCl_5^- , and protonic acid anions including inorganic acid anions such as NO_3^- and SO_4^{2-} , organosulfonic acid anions such as p-toluenesulfonic acid, naphthalene-sulfonic acid, alkyl-substituted sulfonic acid having from 1 to 5 carbon atoms, CF_3SO_3^- and CH_3SO_3^- , and carboxylic acid anion such as CH_3COO^- and $\text{C}_6\text{H}_5\text{COO}^-$. Other examples include

polyelectrolytic anions of the compounds such as polyacrylic acid, polymethacrylic acid, polystyrenesulfonic acid, polyvinylsulfonic acid, polyvinylsulfuric acid, poly- α -methylsulfonic acid, polyethylenesulfonic acid and polyphosphoric acid. However, the present invention is by no means limited thereto. Of these, preferred are anions of a high molecular or low molecular organosulfonic acid compound and a polyphosphoric acid, and more preferred is an anion of an aromatic sulfonic acid compound.

[0024]

The concentration of the monomer represented by formula (I) for use in the production method of a capacitor of the present invention varies depending on the substituent (kind) of the compound or the kind of solvent, however, it is in general preferably from 10^{-3} to 10 mol/l, more preferably from 10^{-2} to 5 mol/l. The reaction temperature is selected according to respective reaction processes and cannot be specifically limited; however, it is generally from -70 to 250°C , preferably from 0 to 150°C and more preferably from 15 to 100°C .

[0025]

The reaction solvent for use in the production method of the present invention may be any solvent as far as it can dissolve the monomer, the oxidizing agent and the electrolyte having a dopant ability individually or

altogether. Examples thereof include tetrahydrofuran (THF), dioxane, ethers such as diethyl ether, aprotic polar solvents such as dimethylformamide, acetonitrile, benzonitrile, N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), esters such as ethyl acetate and butyl acetate, nonaromatic chlorine solvents such as chloroform and methylene chloride, nitro compounds such as nitromethane, nitroethane and nitrobenzene, alcohols such as methanol, ethanol and propanol, organic acids such as formic acid, acetic acid and propionic acid, acid anhydrides of the organic acid (e.g., acetic anhydride), water, and a mixed solvent thereof. The compound may be introduced into the dielectric layer (may be subjected to polymerization) in a solvent system, namely, a two-liquid system or a three-liquid system, where the above-described oxidizing agent and/or the electrolyte having a dopant ability and the monomer are individually dissolved.

[0026]

The solid electric conductor thus produced has an electric conductivity of from 0.1 to 200 S/cm, preferably from 1 to 100 S/cm, more preferably from 10 to 100 S/cm.

[0027]

For one part electrode of the present invention, a known material such as aluminum, titanium, tantalum, niobium, an alloy (having the same valve action) using such

a material as a substrate or a sintered body mainly comprising such a material, is used in the form of a foil or bar. This metal electrode is used after treating the surface thereof by a known method, such as etching or chemical forming, so as to increase the specific surface area, and thereby forming a metal oxide film layer on the metal foil.

[0028]

The solid electrolyte is preferably formed by effecting the formation process on the dielectric layer. In particular, a method of chemically depositing an organic electric conductor having excellent heat resistance on a dielectric material having a porous or void structure is preferred in the present invention. Furthermore, in order to attain good electrical contacting, an electric conductor layer is preferably provided on the semiconductor and the electric conductor layer is formed, for example, by solidifying or plating an electrically conducting paste, sputtering a metal or forming an electrically conducting resin film.

[0029]

The capacitor thus constituted according to the production method of the present invention is jacketed with a resin mold, a resin case or a metal-made jacket case or by resin dipping and then the capacitor can be used as a

product capacitor for various uses.

[0030]

[Examples]

The present invention is described in greater detail below by referring to the Examples and Comparative Examples. (Example 1)

An aluminum foil having a purity of 99.99% and a thickness of 100 μm was used as an anode and the surface thereof was electrochemically etched by an ordinary method to prepare a porous aluminum foil. The porous aluminum foil obtained was subjected to formation in an ammonium adipate solution to form an aluminum oxide layer as a dielectric thin film on the aluminum foil and then boiled in hot water to again effect formation to homogenize the dielectric thin film. The thus-prepared aluminum foil was thoroughly dried and coated with an aqueous solution of 0.1M ferric sulfate as an oxidizing agent on the porous surface, and then dried under heating (at a temperature of 80°C) to support and activate the oxidizing agent. Thereafter, the aluminum foil was dipped in an ethanol solution having dissolved therein 5 g of 1,3-dihydroisothianaphthene and 0.1 g of sodium dodecylbenzenesulfonate (hereinafter simply referred to as "DBSNa") and heated at 80°C for 10 minutes in a vapor phase. This in-situ polymerization accompanied by the evaporation of solvent was repeated 20 times to produce a polymer

composition. The polymer composition deposited on the surface was very carefully measured on the electric conductivity by a four-probe method and found to be 50 S/cm. The capacitor device thus manufactured was measured on the properties and the results obtained are shown in Table 1. The capacity and $\tan \delta$ are the values at a frequency of 120 Hz and the impedance is a value at 1,000 KHz.

[0031]

(Comparative Example 1)

An aluminum foil subjected to formation in the same manner as in Example 1 was dipped in a three-component mixed solution (the monomer, oxidizing agent and dopant were the same) adjusted so that each component had the same concentration as in Example 1 and immediately the in-situ polymerization by heating at 80°C for 10 minutes was repeated 20 times to manufacture a capacitor device. The electric conductivity on the surface was carefully measured by a four-probe method and found to be 10^{-2} S/cm. However, the capacitor formed therefrom had a small capacity and the capacitor properties were not satisfied (shown together in Table 1).

[0032]

(Example 2)

A capacitor device was manufactured by the same production method except for using 1,3-dihydronaphtho[2,3-

c]thiophene in place of 1,3-dihydroisothianaphthene used in Example 1. The polymer composition deposited on the surface had an electric conductivity of 20 S/cm (by a four-probe method). The capacitor properties were also measured in the same manner. The results obtained are shown in Table 1.

[0033]

(Example 3)

A capacitor device was manufactured through the same process except for using 5,6-dioxymethylene-1,3-dihydroisothianaphthene in place of 1,3-dihydroisothianaphthene used in Example 1 and using a monomer solution not containing the dopant (DBSNa) described in Example 1. The processing conditions in the in-situ polymerization were 50°C and 10 minutes. The polymer composition deposited on the surface had an electric conductivity of 80 S/cm (by a four-probe method). The capacitor properties obtained are shown in Table 1.

[0034]

(Comparative Example 2)

An aluminum foil prepared in the same manner as in Example 1 was dipped in a mixed component solution containing the same monomer and oxidizing agent as in Example 3 adjusted so that each component had the same concentration as in Example 3, and then the processing was performed under the same conditions (50°C, 10 minutes) in

the same repetitions as in Example 3 to manufacture a capacitor device. The electric conductivity on the surface was 0.1 S/cm and with respect to the capacitor properties, the capacity was small (shown together in Table 1).

[0035]

(Example 4)

A capacitor device was manufactured by the same production method as in Example 1 except for using 1,3-dihydrothieno[3,4-b]quinoxaline in place of 1,3-dihydroisothianaphthene used in Example 1 and using sodium naphthalenesulfonate (hereinafter simply referred to as "NSNa") in place of dodecylbenzenesulfonic acid as a dopant. The polymer composition deposited on the surface had an electric conductivity of 5 S/cm (by a four-probe method). The capacitor properties were measured and the data obtained are shown in Table 1.

[0036]

(Example 5)

A capacitor device was manufactured by the same production method as in Example 1 except for using 5,6-dimethoxy-1,3-dihydroisothianaphthene in place of 1,3-dihydroisothianaphthene used in Example 1 and using NSNa in place of DBSNa. The polymerization temperature and time were changed to 70°C and 20 minutes. The polymer composition deposited on the surface had an electric

conductivity of 80 S/cm (by a four-probe method). The capacitor properties were measured and the results obtained are shown in Table 1.

[0037]

[Table 1]

Capacitor Properties

	Capacity (μF)	$\tan \delta$ (%)	Leakage Current ($\mu\text{A} \cdot 10 \text{ V value}$)	Impedance (Ω)
Example 1	9.9	0.88	0.09	0.078
Example 2	9.8	0.92	0.08	0.092
Example 3	10.1	0.80	0.08	0.052
Example 4	9.9	0.95	0.06	0.080
Example 5	10.2	0.86	0.06	0.055
Comparative Example 1	4.8	2.50	10.50	0.95
Comparative Example 2	6.7	2.30	8.65	0.67

[0038]

(Comparative Example 3)

The every 10 capacitors manufactured according to the production methods of Examples 1 to 5, Comparative Examples 1 and 2 were compared on the properties between before and after the reflow processing.

[Table 2]

Results of Test on Reflow Heat Resistance
(number of products accepted per 10 devices)

	Before Reflow Processing	After Reflow Processing
Device produced in Example 1	10	10
Device produced in Example 2	9	7
Device produced in Example 3	10	9
Device produced in Example 4	10	10
Device produced in Example 5	10	10
Device produced in Comparative Example 1	3	0
Device produced in Comparative Example 2	2	1

[0039]

(Reference Example 1)

A 1,3-dihydroisothianaphthene monomer (melting point: 23°C) was solution-polymerized in nitrobenzene at 50°C in the presence of oxygen and ferric chloride (oxidizing agent) according to the method described in Synthetic Metals, Vol. 16, pp. 379-380 (1986) and the polymer obtained was measured on the electric conductivity. The electric conductivity was as low as 0.1 S/cm and the polymer was not suitable for the solid electrolyte of a capacitor.

[0040]

[Effects of the Invention]

The solid electrolytic capacitor produced by the production method of the present invention is characterized in that a highly electric conducting polymer having excellent heat resistance and capable of being produced by a simple chemical polymerization process is used as a solid electrolyte, and therefore, a heat-resistant solid electrolytic capacitor having high capacity, low impedance and good moisture resistance load can be provided.

[BRIEF DESCRIPTION OF THE DRAWING]

[Fig. 1]

Fig. 1 is a representative longitudinal section of a capacitor using a foil, according to the present invention.

[Description of Numerical References]

- 1 foil
- 2 pore
- 3 aluminum oxide layer
- 4 solid electrolyte
- 5 dielectric layer
- 6 sealing resin
- 7 lead terminal

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To obtain a solid electrolytic capacitor having high capacity, low impedance, good moisture resistance load and excellent heat resistance.

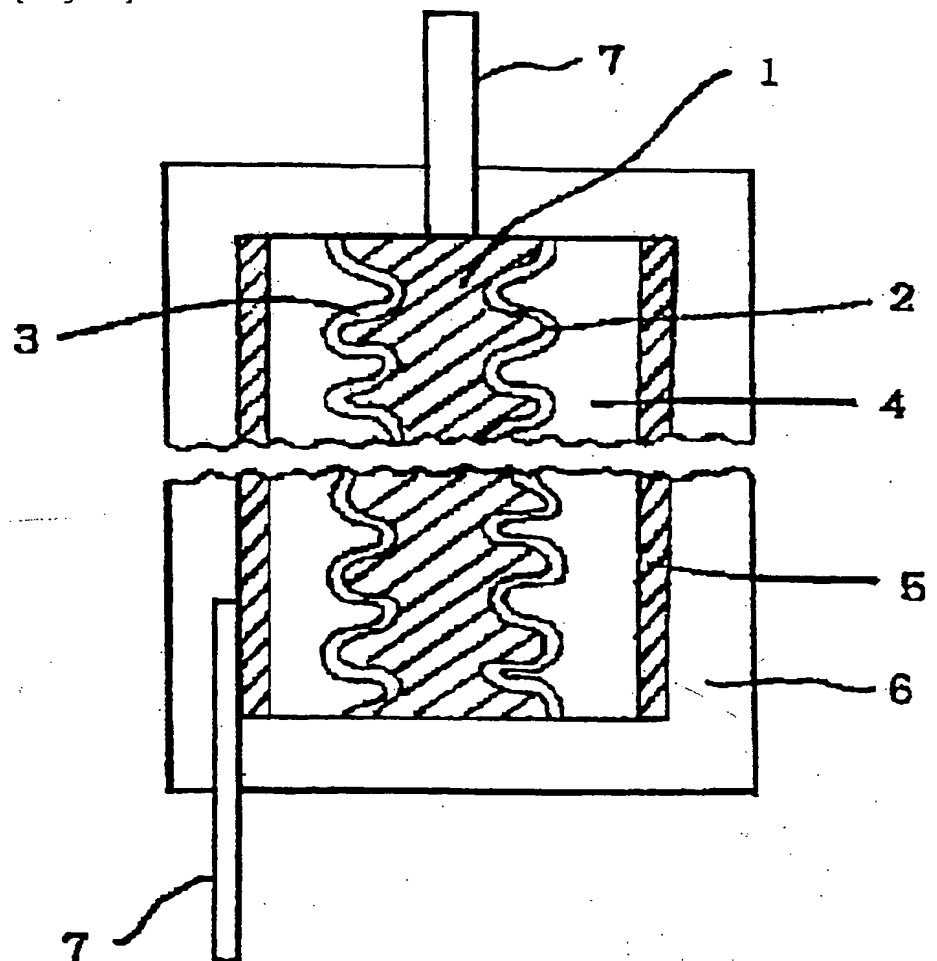
[MEANS TO SOLVE THE PROBLEM]

A method for producing a solid electrolytic capacitor comprising a valve acting metal, an oxide film layer formed on the metal and an electrically conducting polymer composition formed on the surface of the oxide film layer is provided, wherein a condensed heteropolycyclic compound having a specific chemical structure containing a 1,3-dihydrothiophene ring is effectively polymerized by using an oxidizing agent alone or altogether in the presence of another anion having a dopant ability, on or in the vicinity of the surface of the oxide film layer.

[SELECTED DRAWING] None.

[NAME OF DOCUMENT] Drawing

[Fig. 1]



**ATTN: BOX PROVISIONAL PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Provisional Application of

IKENOUE, Yoshiaki and KONUMA, Hiroshi

Provisional Application No.: 60/106,968

Filed: November 4, 1998



For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

SUBMISSION OF VERIFIED ENGLISH TRANSLATION

FILED
MAY 10 1999

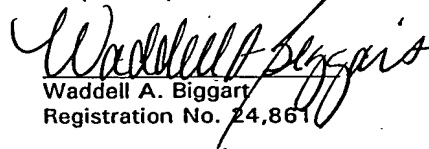
BOX PROVISIONAL PATENT APPLICATION
Attn: Office of National Application Review
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

In view of Applicants provisional application filing on November 4, 1998 in a foreign (Japanese) language, and since Applicants' attorney has not yet received the appropriate "Notice to File Missing Parts of Provisional Application Filed Under 37 CFR 1.53(b)(2)" for the above provisional application, submitted herewith is the verified English language translation (32 pages of specification + 1 pages of drawing(s)) for the above-mentioned provisional application previously filed in the Japanese language. Also enclosed please find a Request for Corrected Provisional Application Filing Receipt.

A check for the statutory fee of \$130.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. 1.16 and 1.17 which may be required during the entire pendency of the provisional application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Respectfully submitted,


Waddell A. Biggar
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB:tnj
Date: May 10, 1999

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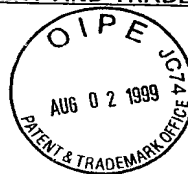
**ATTN: BOX PROVISIONAL PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Provisional Application of

IKENOUE, Yoshiaki and KONUMA, Hiroshi

Provisional Application No.: 60/106,968

Filed: November 4, 1998



For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

BOX PROVISIONAL PATENT APPLICATION

Attn: Office of National Application Review
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Submissions: SUBMISSION OF VERIFIED ENGLISH TRANSLATION; ENGLISH LANGUAGE
VERIFIED TRANSLATION (32 pages + 1 drawing + executed Translator's
Declaration) WITH ACCOMPANYING TRANSLATOR'S DECLARATION; A
CHECK FOR \$ 130.00; REQUEST FOR CORRECTED PROVISIONAL
APPLICATION FILING RECEIPT



PLEASE STAMP AND RETURN TO
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(202) 293-7060

BOX 235X

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Atty/Sec: WAB/tmj
Date: May 10, 1999

0360

ATTN: BOX MISSING PARTS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

IKENOUE, Yoshiaki and KONUMA, Hiroshi

Appln. No. 60/106,968

Filed: November 4, 1998



For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR

LETTER OF CLARIFICATION

BOX MISSING PARTS

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

The undersigned wishes to acknowledge receipt of the Notice to File Missing Parts of Provisional Application Filing Date Granted dated November 4, 1998, copy attached hereto, requiring the submission of the verified English language translation. The Office is advised that the verified English language translation, required in the attached notice, was timely filed on May 10, 1999. A copy of said submission, along with a copy of the date stamped post card receipt reflecting this timely submission, are attached for the Office's records.

Accordingly, in view of the above, all outstanding requirements have been timely met.

Respectfully submitted,


Waddell A. Biggart
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB/tmj

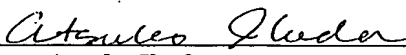
Date: August 2, 1999

DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/106,968 filed on November 4, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 20th day of January, 1999


Atsuko Ikeda

[NAME OF DOCUMENT] Specification

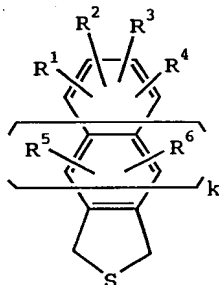
[TITLE OF THE INVENTION]

Method for Producing Solid Electrolytic Capacitor

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for producing a solid electrolytic capacitor, comprising polymerizing a condensed heteropolycyclic compound represented by the following formula (I):

[Chem. 1]



(wherein the substituents R¹, R², R³, R⁴, R⁵ and R⁶ each independently represents a monovalent group selected from the group consisting of H, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a trihalomethyl group, a phenyl group and a substituted phenyl group, the hydrocarbon chains of R¹, R², R³, R⁴, R⁵ and R⁶ may combine to each other at any site to form at

least one divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms to which the substituents are bonded, the alkyl group, the alkoxy group or the alkylester group of R¹, R², R³, R⁴, R⁵ or R⁶ or the cyclic hydrocarbon chain formed by the substituents may contain any of carbonyl, ether, ester, amide, sulfide, sulfinyl, sulfonyl and imino bonds, k represents a number of the condensed ring enclosed by the dihydrothiophene ring and the benzene ring having substituents R¹ to R⁴ and represents an integer of from 0 to 3, and the condensed ring may optionally contain nitrogen or N-oxide) alone or together with another anion having a dopant ability, within a metal oxide dielectric porous layer by the action of an oxidizing agent.

[Claim 2] The method for producing a solid electrolytic capacitor as claimed in claim 1, wherein the condensed heteropolycyclic compound uses at least one monomer selected from dihydroisothianaphthene, dihydronaphtho[2,3-c]thiophene and dihydrothieno[3,4-b]quinoxaline derivatives.

[Claim 3] The method for producing a solid electrolytic capacitor as claimed in claim 1, wherein the condensed heteropolycyclic compound uses at least one monomer selected from 1,3-dihydroisothianaphthene, 5,6-

dioxymethylene-1,3-dihydroisothianaphthene, 5,6-dimethoxy-1,3-dihydroisothianaphthene, 1,3-dihydronaphtho[2,3-c]-thiophene, 1,3-dihydrothieno[3,4-b]quinoxaline and 1,3-dihydrothieno[3,4-b]quinoxaline.

[Claim 4] The method for producing a solid electrolytic capacitor as claimed in claims 1 to 3, wherein the polymer production process is repeated more than at least twice within the same dielectric layer.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method for producing a solid electrolytic capacitor containing a specific electrically conducting polymer composition as the solid electrolyte, more specifically, the present invention relates to an electrolytic capacitor capable of realizing miniaturization, high capacity and low impedance of the electrolytic capacitor and having good moisture resistance load and excellent heat resistance.

[0002]

[Background Art]

A solid electrolytic capacitor comprises an anode substrate comprising a metal foil subjected to etching treatment and having a large specific surface area. A basic device of the capacitor is manufactured by forming an oxide

dielectric film layer on the anode substrate, a solid semiconductor layer (hereinafter simply referred to as a solid electrolyte) as an opposing electrode outside the dielectric layer and preferably further an electric conductor layer such as an electrically conducting paste. Then, the device as a whole is completely sealed by an epoxy resin or the like and put into use as a capacitor part in electric products over a wide range.

[0003]

Of these basic elements, for the solid electrolyte, it has been heretofore known to use, for example, an inorganic semiconductor material such as manganese dioxide and lead dioxide or an electrically conducting organic material containing a TCNQ complex salt or a π -conjugated polymer such as polyaniline (JP-A-61-239617 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), polypyrrole (JP-A-61-240625), polythiophene (JP-A-2-15611), polyisothianaphthene containing no dopant (JP-A-62-118509) or polyisothianaphthene in the doped state (JP-A-62-118511).

[0004]

[Problems to Be Solved by the Invention]

As the method for forming a solid electrolyte layer, a method of fusing a solid electrolyte into a porous or void structure of a dielectric layer on a metal surface to form

a solid electrolyte layer on the dielectric layer and a method of producing a solid electrolyte on a dielectric layer have been conventionally known.

[0005]

[Means to Solve the Problems]

As the electronic equipment is recently reduced in the weight, a compact capacitor having a high capacity, excellent high-frequency properties and a low impedance is being demanded. To cope with this, it has been heretofore attempted to form a solid electrolyte of various types on a dielectric film. Of these, electrically conducting metal oxides and electrically conducting polymers are drawing an attention. One of the reasons therefor is because the solid electrolyte may be improved to have a sufficiently high electric conductivity. However, there is a problem in that if the electric conductivity is higher than a proper range, the leakage current value greatly increases to cause short circuit, whereas if it is lower than the proper range, the frequency properties are deteriorated to cause large reduction in the capacity. Accordingly, a matter of problem to be studied and solved is to control a proper range of the electric conductivity and attain thermal stability of the solid electrolyte.

[0006]

To speak more specifically, conventional capacitors

using an electrically conducting polymer such as polypyrrole have a problem in that the capacitor properties greatly fluctuate according to the moisture resistance load. In this concern, the demand for heat resistance is keenly increased. For example, heat resistance in soldering (reflow property) at the time of forming a capacitor part from a capacitor device is important and a capacitor device having high heat resistance is being demanded. Conventional techniques are not satisfied with respect to the solid electrolyte and the production method thereof.

[0007]

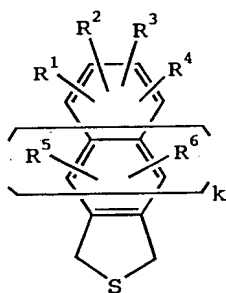
[Mode for Carrying Out the Invention]

As a result of extensive investigations to solve the above-described problems, the present inventors have first found that when a solid electrolytic capacitor is produced by polymerizing a condensed heteropolycyclic compound having a specific chemical structure on or in the vicinity of the surface of a metal oxide dielectric layer having a porous structure, a capacitor excellent in the reflow heat resistance and the like is produced. The present invention has been accomplished based on this finding.

[0008]

That is, the present invention provides a solid electrolytic capacitor using as a solid electrolyte a polymer composition obtained by introducing a condensed

heteropolycyclic compound represented by the following formula (I):



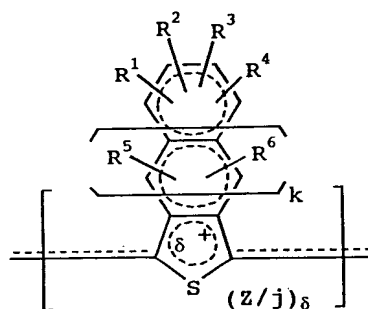
(wherein the substituents R^1 , R^2 , R^3 , R^4 , R^5 and R^6 each independently represents a monovalent group selected from the group consisting of H, a linear or branched, saturated or unsaturated alkyl, alkoxy or alkylester group having from 1 to 10 carbon atoms, a halogen, a nitro group, a cyano group, a primary, secondary or tertiary amino group, a trihalomethyl group, a phenyl group and a substituted phenyl group, the hydrocarbon chains of R^1 , R^2 , R^3 , R^4 , R^5 and R^6 may combine to each other at any site to form at least one divalent chain for forming at least one 3-, 4-, 5-, 6- or 7-membered saturated or unsaturated hydrocarbon cyclic structure together with the carbon atoms to which the substituents are bonded, the alkyl group, the alkoxy group or the alkylester group of R^1 , R^2 , R^3 , R^4 , R^5 or R^6 or the cyclic hydrocarbon chain formed by the substituents may contain any of carbonyl, ether, ester, amide, sulfide,

sulfinyl, sulfonyl and imino bonds, k represents a number of the condensed ring enclosed by the dihydrothiophene ring and the benzene ring having substituents R' to R' and represents an integer of from 0 to 3, and the condensed ring may optionally contain nitrogen or N-oxide) alone or together with another anion having a dopant ability, into a metal oxide dielectric porous layer (on or in the vicinity of the surface of the porous structure) and acting thereon an oxidizing agent, and also provides a production method of the electrolytic capacitor. The in-situ chemical polymerization reaction within the dielectric layer may be caused by introducing an oxidizing agent simultaneously with a condensed heteropolycyclic compound or further with an anion or by first introducing an oxidizing agent into the surface of the dielectric layer and then introducing a condensed heteropolycyclic compound alone or together with an anion.

[0009]

The present invention further provides a solid electrolytic capacitor, wherein the polymer composition obtained by the above-described production process is an electrically conducting polymer composition having a chemical structure of containing in the main chain at least one structural unit represented by the following formula (II):

[Chem. 3]



(wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and k are the same as in formula (I), provided that when $k=0$, derivatives having a chemical formula where the substituents R^1 to R^6 all are H are excluded, the condensed ring may optionally contain nitrogen or N-oxide, δ is from 0 to 1, Z represents an anion, and j represents a valency number of Z and is 1 or 2), and also provides a production method of the electrolytic capacitor.

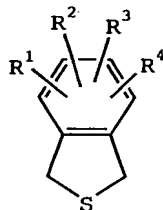
[0010]

More specifically, the present invention relates to a solid electrolytic capacitor comprising electrodes opposing to each other, a dielectric layer formed on the surface of one electrode and having a metal oxide porous structure, and a solid electrolyte formed on the dielectric layer and comprising a polymer composition obtained by the above-described production process, as well as to a production method of the electrolytic capacitor.

[0011]

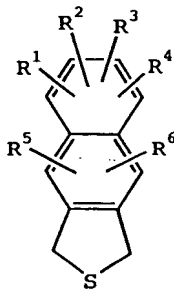
The condensed heteropolycyclic compound represented by formula (I) is specifically a derivative having a 1,3-dihydroisothianaphthene (or also called 1,3-dihydrobenzo-[c]thiophene) skeleton represented by the following formula (III):

[Chem. 4]



(wherein R¹, R², R³ and R⁴ are the same as in formula (I), and the condensed ring may optionally contain nitrogen or N-oxide) or a derivative having a 1,3-dihydronaphtho[2,3-c]thiophene skeleton represented by the following formula (IV):

[Chem. 5]



(wherein the substituents R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are the same as in formula (I), and the condensed ring may optionally contain nitrogen or N-oxide). Other examples include a derivative having a 1,3-dihydroanthra[2,3-c]thiophene skeleton and a derivative having a 1,3-dihydronaphthaceno[2,3-c]thiophene skeleton.

[0012]

Furthermore, derivatives, in which two adjacent substituents among the substituents R^1 , R^2 , R^3 and R^4 in the condensed heteropolycyclic compound represented by formula (I) are combined to each other through an unsaturated bond to newly form a condensed 6-membered ring (ortho-substitution), may also be used and specific examples thereof include, when $k=0$, a 1,3-dihydronaphtho[1,2-c]thiophene derivative, when $k=1$, a 1,3-dihydrophenanthra[2,3-c]thiophene derivative and a 1,3-dihydrotriphenylo[2,3-c]thiophene derivative, and when $k=2$, a 1,3-dihydrobenzo[a]anthraceno[7,8-c]thiophene derivative.

[0013]

The condensed ring in the condensed heteropolycyclic compound represented by formula (I) may optionally contain nitrogen or N-oxide and examples of such a condensed ring include, when $k=0$, 1,3-dihydrothieno[3,4-b]quinoxaline, 1,3-dihydrothieno[3,4-b]quinoxaline-4-oxide and 1,3-dihydrothieno[3,4-b]quinoxaline-4,9-dioxide.

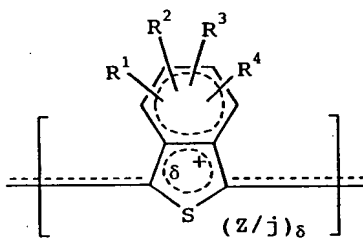
[0014]

As described in the foregoing, the condensed heteropolycyclic compound represented by formula (I) has the above-described 1,3-dihydro-type condensed heteropolycyclic compound skeleton and can easily provide an electrically conducting polymer composition by the oxidation reaction process described in the present invention. Representative examples of the compound having a simple chemical formula are described later (Compound (a) to Compound (t)). R^1 , R^2 , R^3 , R^4 , R^5 and R^6 in formula (I) each independently represents a substituted phenyl group. The substituted phenyl group includes a structure such that at least one monovalent group selected from Cl, Br, I, F and CF_3 is bonded as a substituent to a phenyl ring.

[0015]

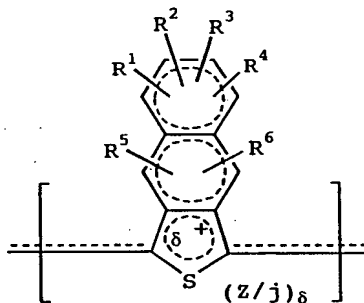
The polymer composition obtained by the above-described production process of a polymer preferably has a chemical structure of formula (II) where $k=0$, namely, formula (V):

[Chem. 6]



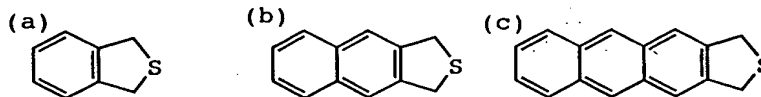
(wherein R^1 , R^2 , R^3 , R^4 , δ , Z and j are the same as in formula (II), and the condensed ring may optionally contain nitrogen or N-oxide) or where $k=1$, namely, formula (VI):

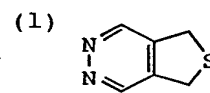
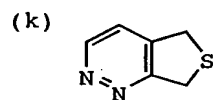
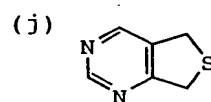
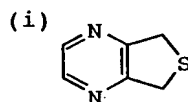
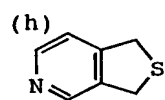
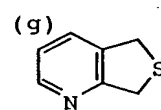
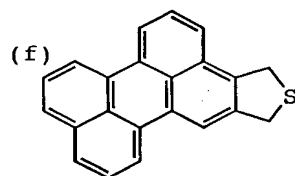
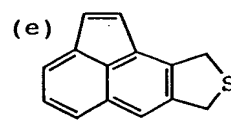
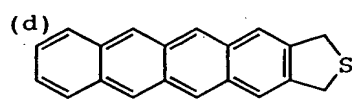
[Chem. 7]



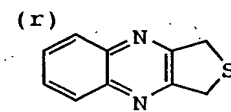
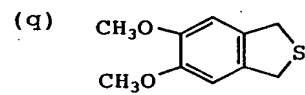
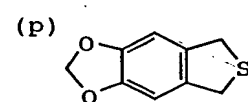
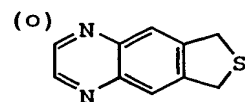
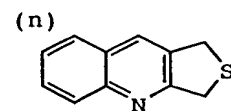
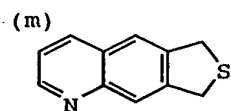
(wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , δ , Z and j are the same as in formula (II), and the condensed ring may optionally contain nitrogen or N-oxide).

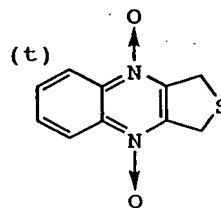
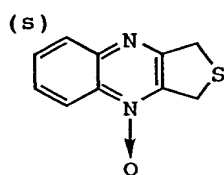
[Chem. 8]





[Chem. 9]





[0016]

The polymerization process according to the present invention is characterized in that the oxidative dehydrogenation reaction (polymerization reaction) of the condensed heteropolycyclic compound takes place within pores of a metal oxide dielectric layer and further that due to such an environment in using an oxidizing agent, the oxidizing agent is more activated (accelerates the polymerization reaction) to provide a polymer composition having a high electric conductivity. These characteristic features have been found as a result of evaluating the capacitor properties (e.g., capacity, $\tan \delta$, leakage current, impedance, reflow heat resistance). In other words, according to the production process of a solid polyelectrolyte (polymer composition) of the present invention, the dehydrogenative oxidation reaction (4 electron oxidation) of the condensed heteropolycyclic compound can be effectively achieved on or in the vicinity of the surface of a metal oxide in the presence or absence of a solvent under short-time and simple reaction.

conditions. Therefore, as compared with the case using a conventionally known dehydrogenative oxidation reaction of a pyrrole or a thiophene (in this case, 2 electron oxidation polymerization), industrially useful solid electrolytic capacitor properties can be provided. The effect of accelerating the in-situ chemical polymerization in the dielectric layer may be considered to come out due to the complicated finely porous structure or large specific area of the dielectric or due to the surface free energy of the oxide thin film, however, the principle thereof is not yet elucidated.

[0017]

With respect to conventionally known examples of the method for producing a polymer, JP-A-63-118323 and JP-A-2-242816 disclose a method of oxidatively polymerizing a monomer having a 1,3-dihydroisothianaphthene structure in the presence of an oxidizing agent. This is, however, an example of a mere polymerization method in the polymer chemistry and the above-described patent publications are completely silent on the chemical reaction process (in-situ chemical polymerization process) using the effect on the surface of a metal oxide described in the present invention. Synthetic Metals, Vol. 16, pp. 379-380 (1986) discloses a method of oxidatively polymerizing a monomer having a 1,3-dihydroisothianaphthene structure in the presence of oxygen

and an oxidizing agent together, but this is also an example of mere synthesis reaction. Furthermore, JP-A-62-118509 and JP-A-62-118511 disclose use of an electrochemically polymerized polymer as a solid electrolyte and thus, these patent publications differ in the production process from the present invention. Moreover, the capacitor properties are different from those in the present invention.

[0018]

As the second object of the present invention, a method capable of achieving high capacity is provided. That is, according to the present invention, an oxidizing agent is charged together with the monomer alone or further with another anion having a dopant ability and by performing step by step the dehydrogenative 4 electron oxidation reaction (polymerization) directly within a metal oxide foil (for example, an formed aluminum foil), a polymer composition can be effectively filled into and formed within the foil. More specifically, the polymerization of a condensed heteropolycyclic compound proceeds through such a process that an oxidizing agent is carried and activated on the surface of a metal oxide having a porous structure by the coating according to a solution process or by the sublimation or evaporation according to a vapor phase process and then a condensed heteropolycyclic compound is

introduced into the surface of the fine structure, if desired, together with a compound capable of donating another anion having a dopant ability, thereby forming the polymer composition on or in the vicinity of the dielectric. By repeating this process step by step, a solid electrolyte comprising the polymer composition can be effectively filled and formed inside the pores. Due to this, homogeneity in the electric conducting path within the solid electrolyte layer can be remarkably improved, unnecessary formation of stresses inside the pores can be prevented (prevention of rupture of the dielectric layer) and as a result, excellent capacitor properties including high capacity and low impedance can be realized.

[0019]

As the third object of the present invention, a method capable of ensuring excellent soldering heat resistance (heat stability) is provided. Conventionally known capacitors using a solid electrolyte comprising polypyrrole or the like undergo large fluctuation in the LCR value at a high temperature and a high humidity and has poor reliability. However, the electrically conducting composition having a chemical formula shown in the present invention has excellent heat stability and exhibits good stability in the doped state. Furthermore, this polymer composition is step by step deposited on the surface of a

dielectric and accordingly, a structure of many polymer composition thin films being overlapped can be formed. Thus, the polymer can prevent damages of the dielectric film and a capacitor having excellent heat stability can be provided.

[0020]

The oxidizing agent for use in the production method of the present invention may be any oxidizing agent as far as oxidation reaction by dehydrogenative 4 electron oxidation can be satisfactorily effected and the capacitor performance can be improved in the use environment. In practice, compounds which are industrially inexpensive and easy to handle are preferred. Specific examples thereof include Fe(III) compounds such as FeCl_3 , FeClO_4 , and Fe (organic acid anion) salt, anhydrous aluminum chloride/cuprous chloride, alkali metal persulfates, ammonium persulfate salts, peroxides, manganese such as potassium permanganate, quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-1,4-benzoquinone and tetracyano-1,4-benzoquinone, halogens such as iodine and bromine, peracid, sulfuric acid, fuming sulfuric acid, sulfur trioxide, sulfonic acids such as chlorosulfuric acid, fluorosulfuric acid and amidosulfuric acid, ozone, and a combination of a plurality of these oxidizing agents.

[0021]

Examples of the base compound for the organic acid anion constituting the Fe (organic acid anion) salt include an organosulfonic acid, an organocarboxylic acid, an organophosphoric acid and an organoboric acid. Specific examples of the organosulfonic acid include benzenesulfonic acid, p-toluenesulfonic acid, methanesulfonic acid, ethanesulfonic acid, α -sulfonaphthalene, β -sulfonaphthalene, naphthalenedisulfonic acid, alkyl naphthalenesulfonic acid (examples of the alkyl group include butyl, triisopropyl and di-t-butyl, etc.).

[0022]

Specific examples of the organocarboxylic acid include acetic acid, propionic acid, benzoic acid and oxalic acid. Furthermore, in the present invention, a polyelectrolyte anion such as polyacrylic acid, polymethacrylic acid, polystyrenesulfonic acid, polyvinylsulfonic acid, polyvinylsulfuric acid, poly- α -methylsulfonic acid, polyethylenesulfonic acid and polyphosphoric acid may also be used. However, these are described only for the purpose of illustrating examples of the organosulfonic acid and the organocarboxylic acid and the present invention is by no means limited thereto. The counter cation of the above-described anion is not particularly limited in the present invention and examples thereof include H^+ , alkali metal ion

such as Na^+ and K^+ , and ammonium ion substituted by a hydrogen atom, a tetramethyl group, a tetraethyl group, a tetrabutyl group or a tetraphenyl group. Of these oxidizing agents, oxidizing agents containing a trivalent Fe compound, cuprous chloride, a persulfuric acid alkali salt, an ammonium persulfate, a manganic acid or a quinone are suitably used.

[0023]

Examples of the anion having a dopant ability which is allowed to be present together, if desired, in the production process of the polymer composition of the present invention include electrolytic compounds comprised of anion of oxidizing agent (reductant of the oxidizing agent) produced from the above-described oxidizing agent as a counter anion, and other anionic electrolytes. Specific examples thereof include Group 5B element halide anions such as PF_6^- , SbF_6^- and AsF_6^- , Group 3B element halide anions such as BF_4^- , halogen anions such as I^- , Br^- and Cl^- , halogen acid anions such as ClO_4^- , Lewis acid anions such as AlCl_4^- , FeCl_4^- and SnCl_5^- , and protonic acid anions including inorganic acid anions such as NO_3^- and SO_4^{2-} , organosulfonic acid anions such as p-toluenesulfonic acid, naphthalene-sulfonic acid, alkyl-substituted sulfonic acid having from 1 to 5 carbon atoms, CF_3SO_3^- and CH_3SO_3^- , and carboxylic acid anion such as CH_3COO^- and $\text{C}_6\text{H}_5\text{COO}^-$. Other examples include

polyelectrolytic anions of the compounds such as polyacrylic acid, polymethacrylic acid, polystyrenesulfonic acid, polyvinylsulfonic acid, polyvinylsulfuric acid, poly- α -methylsulfonic acid, polyethylenesulfonic acid and polyphosphoric acid. However, the present invention is by no means limited thereto. Of these, preferred are anions of a high molecular or low molecular organosulfonic acid compound and a polyphosphoric acid, and more preferred is an anion of an aromatic sulfonic acid compound.

[0024]

The concentration of the monomer represented by formula (I) for use in the production method of a capacitor of the present invention varies depending on the substituent (kind) of the compound or the kind of solvent, however, it is in general preferably from 10^{-3} to 10 mol/l, more preferably from 10^{-2} to 5 mol/l. The reaction temperature is selected according to respective reaction processes and cannot be specifically limited, however, it is generally from -70 to 250°C , preferably from 0 to 150°C and more preferably from 15 to 100°C .

[0025]

The reaction solvent for use in the production method of the present invention may be any solvent as far as it can dissolve the monomer, the oxidizing agent and the electrolyte having a dopant ability individually or

altogether. Examples thereof include tetrahydrofuran (THF), dioxane, ethers such as diethyl ether, aprotic polar solvents such as dimethylformamide, acetonitrile, benzonitrile, N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), esters such as ethyl acetate and butyl acetate, nonaromatic chlorine solvents such as chloroform and methylene chloride, nitro compounds such as nitromethane, nitroethane and nitrobenzene, alcohols such as methanol, ethanol and propanol, organic acids such as formic acid, acetic acid and propionic acid, acid anhydrides of the organic acid (e.g., acetic anhydride), water, and a mixed solvent thereof. The compound may be introduced into the dielectric layer (may be subjected to polymerization) in a solvent system, namely, a two-liquid system or a three-liquid system, where the above-described oxidizing agent and/or the electrolyte having a dopant ability and the monomer are individually dissolved.

[0026]

The solid electric conductor thus produced has an electric conductivity of from 0.1 to 200 S/cm, preferably from 1 to 100 S/cm, more preferably from 10 to 100 S/cm.

[0027]

For one part electrode of the present invention, a known material such as aluminum, titanium, tantalum, niobium, an alloy (having the same valve action) using such

a material as a substrate or a sintered body mainly comprising such a material, is used in the form of a foil or bar. This metal electrode is used after treating the surface thereof by a known method, such as etching or chemical forming, so as to increase the specific surface area, and thereby forming a metal oxide film layer on the metal foil.

[0028]

The solid electrolyte is preferably formed by effecting the formation process on the dielectric layer. In particular, a method of chemically depositing an organic electric conductor having excellent heat resistance on a dielectric material having a porous or void structure is preferred in the present invention. Furthermore, in order to attain good electrical contacting, an electric conductor layer is preferably provided on the semiconductor and the electric conductor layer is formed, for example, by solidifying or plating an electrically conducting paste, sputtering a metal or forming an electrically conducting resin film.

[0029]

The capacitor thus constituted according to the production method of the present invention is jacketed with a resin mold, a resin case or a metal-made jacket case or by resin dipping and then the capacitor can be used as a

product capacitor for various uses.

[0030]

[Examples]

The present invention is described in greater detail below by referring to the Examples and Comparative Examples. (Example 1)

An aluminum foil having a purity of 99.99% and a thickness of 100 μm was used as an anode and the surface thereof was electrochemically etched by an ordinary method to prepare a porous aluminum foil. The porous aluminum foil obtained was subjected to formation in an ammonium adipate solution to form an aluminum oxide layer as a dielectric thin film on the aluminum foil and then boiled in hot water to again effect formation to homogenize the dielectric thin film. The thus-prepared aluminum foil was thoroughly dried and coated with an aqueous solution of 0.1M ferric sulfate as an oxidizing agent on the porous surface, and then dried under heating (at a temperature of 80°C) to support and activate the oxidizing agent. Thereafter, the aluminum foil was dipped in an ethanol solution having dissolved therein 5 g of 1,3-dihydroisothianaphthene and 0.1 g of sodium dodecylbenzenesulfonate (hereinafter simply referred to as "DBSNa") and heated at 80°C for 10 minutes in a vapor phase. This in-situ polymerization accompanied by the evaporation of solvent was repeated 20 times to produce a polymer

composition. The polymer composition deposited on the surface was very carefully measured on the electric conductivity by a four-probe method and found to be 50 S/cm. The capacitor device thus manufactured was measured on the properties and the results obtained are shown in Table 1. The capacity and $\tan \delta$ are the values at a frequency of 120 Hz and the impedance is a value at 1,000 KHz.

[0031]

(Comparative Example 1)

An aluminum foil subjected to formation in the same manner as in Example 1 was dipped in a three-component mixed solution (the monomer, oxidizing agent and dopant were the same) adjusted so that each component had the same concentration as in Example 1 and immediately the in-situ polymerization by heating at 80°C for 10 minutes was repeated 20 times to manufacture a capacitor device. The electric conductivity on the surface was carefully measured by a four-probe method and found to be 10^{-2} S/cm. However, the capacitor formed therefrom had a small capacity and the capacitor properties were not satisfied (shown together in Table 1).

[0032]

(Example 2)

A capacitor device was manufactured by the same production method except for using 1,3-dihydronaphtho[2,3-

c]thiophene in place of 1,3-dihydroisothianaphthene used in Example 1. The polymer composition deposited on the surface had an electric conductivity of 20 S/cm (by a four-probe method). The capacitor properties were also measured in the same manner. The results obtained are shown in Table 1.

[0033]

(Example 3)

A capacitor device was manufactured through the same process except for using 5,6-dioxymethylene-1,3-dihydroisothianaphthene in place of 1,3-dihydroisothianaphthene used in Example 1 and using a monomer solution not containing the dopant (DBSNa) described in Example 1. The processing conditions in the in-situ polymerization were 50°C and 10 minutes. The polymer composition deposited on the surface had an electric conductivity of 80 S/cm (by a four-probe method). The capacitor properties obtained are shown in Table 1.

[0034]

(Comparative Example 2)

An aluminum foil prepared in the same manner as in Example 1 was dipped in a mixed component solution containing the same monomer and oxidizing agent as in Example 3 adjusted so that each component had the same concentration as in Example 3, and then the processing was performed under the same conditions (50°C, 10 minutes) in

the same repetitions as in Example 3 to manufacture a capacitor device. The electric conductivity on the surface was 0.1 S/cm and with respect to the capacitor properties, the capacity was small (shown together in Table 1).

[0035]

(Example 4)

A capacitor device was manufactured by the same production method as in Example 1 except for using 1,3-dihydrothieno[3,4-b]quinoxaline in place of 1,3-dihydroisothianaphthene used in Example 1 and using sodium naphthalenesulfonate (hereinafter simply referred to as "NSNa") in place of dodecylbenzenesulfonic acid as a dopant. The polymer composition deposited on the surface had an electric conductivity of 5 S/cm (by a four-probe method). The capacitor properties were measured and the data obtained are shown in Table 1.

[0036]

(Example 5)

A capacitor device was manufactured by the same production method as in Example 1 except for using 5,6-dimethoxy-1,3-dihydroisothianaphthene in place of 1,3-dihydroisothianaphthene used in Example 1 and using NSNa in place of DBSNa. The polymerization temperature and time were changed to 70°C and 20 minutes. The polymer composition deposited on the surface had an electric

conductivity of 80 S/cm (by a four-probe method). The capacitor properties were measured and the results obtained are shown in Table 1.

[0037]

[Table 1]

Capacitor Properties

	Capacity (μF)	$\tan \delta$ (%)	Leakage Current ($\mu\text{A} \cdot 10 \text{ V value}$)	Impedance (Ω)
Example 1	9.9	0.88	0.09	0.078
Example 2	9.8	0.92	0.08	0.092
Example 3	10.1	0.80	0.08	0.052
Example 4	9.9	0.95	0.06	0.080
Example 5	10.2	0.86	0.06	0.055
Comparative Example 1	4.8	2.50	10.50	0.95
Comparative Example 2	6.7	2.30	8.65	0.67

[0038]

(Comparative Example 3)

The every 10 capacitors manufactured according to the production methods of Examples 1 to 5, Comparative Examples 1 and 2 were compared on the properties between before and after the reflow processing.

[Table 2]

Results of Test on Reflow Heat Resistance
(number of products accepted per 10 devices)

	Before Reflow Processing	After Reflow Processing
Device produced in Example 1	10	10
Device produced in Example 2	9	7
Device produced in Example 3	10	9
Device produced in Example 4	10	10
Device produced in Example 5	10	10
Device produced in Comparative Example 1	3	0
Device produced in Comparative Example 2	2	1

[0039]

(Reference Example 1)

A 1,3-dihydroisothianaphthene monomer (melting point: 23°C) was solution-polymerized in nitrobenzene at 50°C in the presence of oxygen and ferric chloride (oxidizing agent) according to the method described in Synthetic Metals, Vol. 16, pp. 379-380 (1986) and the polymer obtained was measured on the electric conductivity. The electric conductivity was as low as 0.1 S/cm and the polymer was not suitable for the solid electrolyte of a capacitor.

[0040]

[Effects of the Invention]

The solid electrolytic capacitor produced by the production method of the present invention is characterized in that a highly electric conducting polymer having excellent heat resistance and capable of being produced by a simple chemical polymerization process is used as a solid electrolyte, and therefore, a heat-resistant solid electrolytic capacitor having high capacity, low impedance and good moisture resistance load can be provided.

[BRIEF DESCRIPTION OF THE DRAWING]

[Fig. 1]

Fig. 1 is a representative longitudinal section of a capacitor using a foil, according to the present invention.

[Description of Numerical References]

- 1 foil
- 2 pore
- 3 aluminum oxide layer
- 4 solid electrolyte
- 5 dielectric layer
- 6 sealing resin
- 7 lead terminal

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To obtain a solid electrolytic capacitor having high capacity, low impedance, good moisture resistance load and excellent heat resistance.

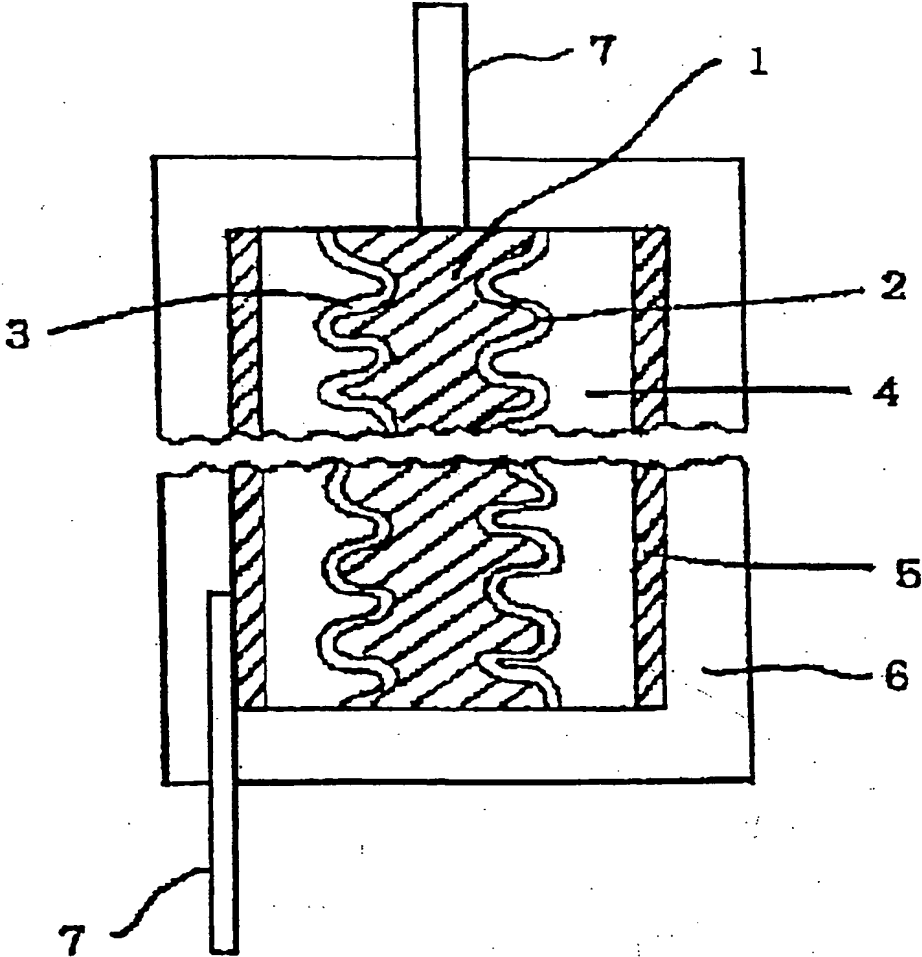
[MEANS TO SOLVE THE PROBLEM]

A method for producing a solid electrolytic capacitor comprising a valve acting metal, an oxide film layer formed on the metal and an electrically conducting polymer composition formed on the surface of the oxide film layer is provided, wherein a condensed heteropolycyclic compound having a specific chemical structure containing a 1,3-dihydrothiophene ring is effectively polymerized by using an oxidizing agent alone or altogether in the presence of another anion having a dopant ability, on or in the vicinity of the surface of the oxide film layer.

[SELECTED DRAWING] None.

[NAME OF DOCUMENT] Drawing

[Fig. 1]



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Konuma et al
Application Number: 60/106968 Filed: 11-4-98
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ATTN: BOX PROVISIONAL APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Provisional Application of

IKENOUE, Yoshiaki and KONUMA, Hiroshi

Provisional Appln. No.: 60/106,968

Filed: November 4, 1998

For: METHOD FOR PRODUCING SOLID ELECTROLYTIC CAPACITOR



SECOND REQUEST FOR CORRECTED PROVISIONAL APPLICATION FILING RECEIPT

ATTN: BOX PROVISIONAL APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

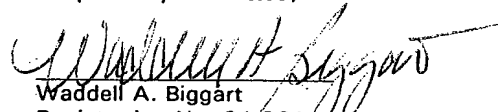
We enclose a copy of the Provisional Application Filing Receipt for the above-identified provisional application and request a correction as follows:

**TITLE METHOD FOR PRODUCING SOLID ELECTROLYTIC
CAPACITOR**

The requested changes are supported by the application transmittal letter filed **November 4, 1998**.

This error was caused by the PTO and therefore no fee is necessary.

Respectfully submitted,


Waddell A. Biggart
Registration No. 24,861

SUGHRUE, MION, ZINN, MACPEAK & SEAS
2100 Pennsylvania Avenue, N.W.
Washington, D.C. 20037-3202
Tel: (202) 293-7060
WAB:tnj
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